Dielectric Screening in Metals and Alloys

A thesis submitted for the degree
of Doctor of Philosophy of
the Australian National University

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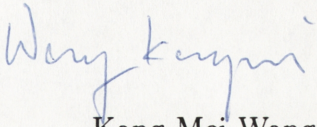
Statement

This thesis reports the work carried out while I was a student in the Department of Theoretical Physics, Research School of Physical Sciences and Engineering of the Australian National University between March 1989 and April 1993, under the supervision of Dr. J. Mahanty with whom I have collaborated in all stages of my research program.

Chapter 1 contains mostly review material, whereas Chapters 2, 3, 4 and 5 comprise my contributions. Some extra mathematical details are included in the Appendices.

None of the work reported here has been submitted to any institution of learning for any degree.



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Abstract

An investigation is made of the total dielectric function of metals and alloys in this thesis. The thesis is divided into two main parts. The first represents an attempt to find a form of the total dielectric function for metals and alloys which is presented in Chapter 2 and 3. The second part, presented in Chapter 4, is concerned with an application relating to the superconducting properties of materials and from the total dielectric function to find their energy gaps through the BCS gap equation.

In the first chapter, an introduction to the dielectric function is given and sets in perspective the relevant theoretical approaches prior to that undertaken in the present work.

A general formalism of the static total dielectric function in metals has been derived following a simple model which gives the dielectric function directly from the equations of motion of the electrons and ions. The interaction between two test charges in a solid is described in terms of a screened Coulomb potential through a total dielectric function that includes electronic and lattice polarisation. The dielectric property of a metal is determined by the free electrons in it, as also by the ions in the lattice positions corresponding to its crystalline structure. The contribution of the ions has two components, one corresponding to their intrinsic induced polarisation, and the other corresponding to the induced polarisation associated with their displacements from equilibrium position. There have been some studies of the total dielectric response of a metal, which incorporates both the electronic and ionic contributions, [see Allen *al al* (1988), Dolgov and Maksimov (1989)].

In the discussion of the total dielectric function, a general form of electronic dielectric function is required; therefore the concept of local-field correction is introduced for completeness in the discussion. When considering the effect from the structure of the ions, van der Waals interaction is considered, that being the dominant non-Coulombic interaction between two ions. The strength of this is determined by the polarisability of the ions. Consideration of the pseudopotentials in electron-ion interaction is included – this turns out to be important to obtain proper results for energy gaps, and is discussed in Chapter 4. As an example, aluminium is studied and the total dielectric function of aluminium is obtained based on different models of local-field corrections which are shown in figures 2.1 to 2.3.

The treatment of alloys in Chapter 3 is similar to that for simple metals in Chapter 2. A total dielectric function is developed for a binary alloy. For transition metals, pseudopotentials play a key role in the form of interaction between electrons and ions. The pseudopotential theory for simple metals is reasonably good, but not so for transition metals. As one of the simplest forms the Ashcroft pseudopotential is used for system. The numerical results of the total dielectric function for the binary alloy NbTa is not given until Chapter 4 in which pseudopotentials are discussed.

Pseudopotential theory is discussed briefly in Chapter 4. The total dielectric functions developed in Chapter 2 and 3 are recalculated including pseudopotentials. The total dielectric function of metals and some alloys is then developed with inclusion of van der Waals interaction and taking into account the contribution of the free electrons, and of the ions through the polarisation associated with their vibrations. With the total dielectric functions, superconducting energy gaps for some materials are evaluated. Results show some improvements; e.g., 4.9% for NbTa and 6.8% for aluminium when the van der Waals interaction is taken into account.

The results for the superconducting energy gaps shown in the thesis are different from these predicted in the BCS theory. It is suggested that this discrepancy could be reduced by invoking the change of the parameters in the electronic dielectric function occurring in the local field correction and by properly choosing the form

of the pseudopotential.

Most of material presented in chapter 2 has been published as:

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The total dielectric function of a metallic crystal

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Contents

CHAPTER 1

Introduction to the dielectric function

1.1 Some remarks

The study of dielectric properties is one of the most important topics of condensed matter physics. The dielectric function together with the magnetic permeability of a medium are associated with the response functions, which describe the response of the medium to various external electromagnetic influences. They are sources of information not only about the direct results of the external action on the medium but also about its internal structure and properties.

The theory of dielectric properties has undergone considerable evolution over the last two hundred years. In the early years, when measurement of electrical and magnetic properties of a medium were not very accurate, its dielectric properties were described in terms of its "dielectric constant", which was a dimensionless number. It is now more appropriate to the dielectric properties of the medium by a "dielectric function", which is a tensor function of the frequency and wave number of the external field, of the ambient temperature and pressure, etc. Considerable progress has been made over the last decades both in the understanding of the general properties of the dielectric function and in the calculation of this quantity for many classes of media. Some pioneers who worked on the dielectric properties of the electron gas are Lindhard, Bohm, Pines, Nozières, and many others during this period. For the electron gas the dielectric function in the so-called Random Phase Approximation (RPA) has been the standard reference basis for further improvements. There are a large number of problems that have not as yet been solved and remain an area of vigourous activity in investigation of the condensed state. One

such area is the theory of superlattices which has developed in recent decades [see Raj and Tilley (1989) in Modern problems in condensed matter sciences vol.24]. This thesis deals with an investigation of the total dielectric function of metals and some alloys, taking into account the contributions of the free electrons, and of the ions through the polarisation associated with their vibrations.

1.2 General considerations

The interaction between two test charges in a solid can be described in terms of a total dielectric function that includes the effects of electronic and lattice polarisation. To calculate the total dielectric function in a medium region of wave vector $\mathbf{k}$, the key point is to have a good electronic dielectric function.

1.2.1 Electronic dielectric function

The calculation of many properties of simple metals is based on the *jellium model.* In this model, one studies the interaction among the electrons themselves, whereas the lattice of positive metal ions is replaced by a rigid uniform background. The large amount of research on this system is due to its conceptual simplicity. The main reason for the persisting interest in this model is the fact that in many metals, the conduction electrons approximately have a homogeneous distribution in space. Furthermore many theories for inhomogeneous systems use the jellium model as a starting point for further investigations. A basic quantity for the study of the jellium model is the frequency and wave vector dependent longitudinal electronic dielectric function $\varepsilon_e(\mathbf{q},\omega)$, which not only allows the study of the electronic dielectric response but also the calculation of several other properties, such as the ground state energy, the dynamic structure factor $S(\mathbf{q},\omega)$, the pair correlation function $g(r)$ [see Lindhard (1954), Bohm and Pines (1953) and Pines and Nozières (1966)].

The two limiting cases which have been studied in sufficient detail are for high and low densities. The concepts of high and low densities themselves are defined here in the natural quantum scales, where the length unit is the Bohr radius a_o and the density unit is a_o^{-3}. For the electron gas at high densities, (i.e., $na_o^3 \gg 1$, n being the number density of electrons), the polarisability can be calculated directly

and rather precisely and is given by the Lindhard formula, [see Lindhard (1954)]

$$\chi_o(\mathbf{k},\omega) = \frac{e^2 m P_F}{2\pi\hbar^3|\mathbf{k}|^2}\left\{1+\frac{\zeta}{2}ln\left[\frac{(1-\zeta)^2-\xi^2}{(1+\zeta)^2-\xi^2}\right]+\frac{1-\zeta^2-\xi^2}{4\xi}ln\left[\frac{(1+\xi)^2-\zeta^2}{(1-\xi)^2-\zeta^2}\right]\right\}. \tag{1.1}$$

Here $P_F = \hbar[3\pi^2 n]^{1/3}, \xi = |\mathbf{k}|/2P_F$, and $\zeta = \omega m/|\mathbf{k}|P_F$. This expression and its various modifications have become the basis of all the subsequent theories of the electron liquid. It does not take into account the effects of the correlation between particles, and the difference between the local field and the average field since, in the limit under consideration these effects are small. Therefore, all the modifications of the Lindhard formula that have been proposed aim at extending this formula to the region of moderate densities by taking into account approximately the short-range correlations between electrons.

On the other hand, in the limit of small densities, $na_o^3 \ll 1$, the spatially homogeneous state proves to be unstable. As was originally shown by Wigner [see Wigner (1934) and Wigner (1938)], the electrons then are localised in the neighbourhoods of the points of a certain crystalline lattice, and the so-called Wigner crystal is thus formed. Here the presence of a spatially homogeneous, rigid substrate with a compensating positive charge is assumed. Actually, of course, when account is taken of the discrete structure of positive charges in the low density limit the system is transformed into a gas of neutral atoms. However, for the analysis of the general properties of the theory of many-electron systems and also for the description of certain particular systems, the concept of the Wigner crystal turns out to be very fruitful.

However, in real condensed media the electron densities are in the intermediate region $na_o^3 \sim 1$. In this case, it is hard to develop a satisfactory theory for electron dielectric function. In order to make some practical progress, many approaches based on various approximations, including direct numerical simulation, have been proposed and used. The electron local-field correction is introduced in the discussion of electron dielectric function for use in this intermediate density region, and will be discussed further in this thesis.

1.2.2 Local-field correction in a electronic system

In the long-wavelength limit, the RPA basically succeeds in explaining the dispersion of the energy of the collective excitations, and in combining the ideas of screening, collective excitations and single-particle excitations. However the RPA is less satisfactory whenever short-range correlations are important. This failure of the RPA in the short-range description of the electron-electron interactions is also reflected in the fact that the pair correlation function $g(r)$, as obtained from the RPA dielectric function, becomes negative near the origin for metallic densities [see Glick and Ferrell (1960)]. There are some other examples of failure, see Miliotis (1971), Platzman and Eisenberger (1974), Batson *et al* (1976), Gibbons *et al* (1976) and Schnatterly (1979). A large variety of approximations has been proposed to improve upon the RPA. In these approximations an electronic local-field correction $G(\mathbf{q},\omega)$ is introduced. This is determined from many-body theory and is intended to describe the exchange and correlation potential on each electron, due to the other electrons. In this case the electric dielectric function is usually written in the form:

$$\varepsilon_e(\mathbf{q},\omega) = 1 - \frac{V(\mathbf{q})\chi_o(\mathbf{q},\omega)}{1 + V(\mathbf{q})\chi_o(\mathbf{q},\omega)G(\mathbf{q},\omega)}. \tag{1.2}$$

The Lindhard function $\chi_o(\mathbf{q},\omega)$ and the RPA dielectric function (with no local field correction) are related via:

$$\varepsilon_{RPA}(\mathbf{q},\omega) = 1 - V(\mathbf{q})\chi_o(\mathbf{q},\omega), \tag{1.3}$$

where the $V(\mathbf{q})$ is a bare Coulomb potential. There has not been much work done to include the frequency dependence in $G(\mathbf{q},\omega)$. The interest in the explicit frequency dependence of $G(\mathbf{q},\omega)$ was rather exceptional [see Dekeyser (1968)], and restricted to some limiting cases. However the dynamics of the exchange and correlation hole became an important topic, in view of the more accurate measurements of the dynamical structure factor at large wave vector, and because sum rules and

causality arguments revealed that a static treatment of $G(\mathbf{q},\omega)$ necessarily leads to theoretical inconsistencies; for details see Kimball (1976), Niklasson (1974) and Kugler (1975). A variety of different approaches has been used to derive expressions for $G(\mathbf{q},\omega)$. But not many explicit calculations of the full frequency and wave vector dependence have been performed. Brosens *et al* (1976) had been involved in one of the calculations of the explicitly frequency dependent $G(\mathbf{q},\omega)$ which was based on the equation of motion for the Wigner distribution function.

Most studies concentrated on the static form $G(\mathbf{q})$ of $G(\mathbf{q},\omega)$ which has often been used for the dynamic dielectric function. Notable in this field are the contributions of Hubbard (1957,1958), Geldart and Vosko (1966), etc. and most recently Gorobchenko *et al.* (1989) and Sjölander (1992) have also made some contribution. These results are used in this thesis, and the total dielectric function is evaluated from first principles using some of the above results for the electron gas. The calculation of the total dielectric function is highly dependent on the choice of the form of the electron local-field correction and the selection of a pseudopotential between the electrons and ions, which will be discussed later.

1.2.3 Basic assumptions of pseudopotential

Not only in solid state physics, but also in the physics of atoms and molecules, it is well known that the chemical bond between atoms is essentially determined by the valence electrons of the atoms, i.e. the electrons in the outer shells. The electrons in the fully occupied shells, i.e. the core electrons, essentially do not contribute to the chemical bond. The periodicity in the table of the chemical elements is based on the fact that the core electrons are (to a first approximation) chemically inactive. This does not mean that the core electrons are unimportant in atomic, molecular and condensed matter physics. They determine the actual states and energies of the valence electrons. Therefore, in a quantum mechanical description of the electronic structure of atoms, molecules or solids, these core electrons have to be included in the Hamiltonian especially for large atoms. For example, an atom with nuclear charge $Z_a e$ and N electrons has the Hamiltonian (neglecting external fields, spin-orbit and other corrections)

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} - Z_a e^2 \sum_{j=1}^{N} \frac{1}{r_j} + \frac{e^2}{2} \sum_{j=1}^{N} \sum_{i \neq j}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{1.4}$$

As is well known, the Schrödinger equation with only one electron in the Coulomb field of a nucleus can be solved. For He, with two electrons, the ground state energy can be calculated variationally with reasonable accuracy by relatively simple analytical techniques. For Li, with 3 electrons, a variational treatment with analytical methods becomes already quite complicated. For atoms with many electrons (say 11 or more), one has to rely on numerical techniques. However if one realizes that core electrons are essentially inactive, and remain intimately bound to their nucleus, for example in NaCl one has to deal with 28 electrons and only 8 out of them determine the chemical bond, one can try to avoid the calculation of the core states over and over again, especially in calculations for complex molecules and alloys. One of the important techniques to take advantage of this core stability is the pseudopotential method. It has been applied to many problems in condensed matter physics and chemistry e.g. the study of the electronic structure of atoms [see Animalu and Heine (1965)], molecules [see Ho et al (1977)] and solids [see Harrison (1966) and Heine et al (1970)], the chemical bond at a surface [see Schlüter et al (1975)], structure and phase-transitions [see Harrison (1966) and Stroud and Ashcroft (1971)], and electron coupling in superconductivity [see Allen and Cohen (1969)].

The pseudopotential concept along with its applications has been an extremely active area [see Harrison (1966), Harrison (1980) and Heine (1970) and Cohen *et al* (1970)]. It is not easy to recover the basic ideas and assumptions behind many models which have been developed, and we shall not attempt that in this thesis.

1.3 The response of a system

The response functions, which describe the response of the system to various external influences (electromagnetic, mechanical, thermal, etc.) and can be described in words as

Response of medium = (Response function) × (Influence).

In this thesis I shall be concerned with the electromagnetic response function, which serves as a concentrated source of information on the results of the action on the medium of external charges and currents. Over more than one hundred years the investigation of electromagnetic response has been and remains to be the main source of information on the microscopic nature of matter in the condensed state at the microscopic level.

1.4 The structure of a system

We start this section with a discussion of the properties of metals and alloys. Metals are monatomic and are different from alloys which have more than one species of atoms. Both of them contain electrons which are in some sense free to move. Both of them contain many common characters. For simplicity, metals are discussed hereafter, and then the difference between them and alloys are specified. The term 'crystalline' mentioned early refers to a substance which has regular molecular/atomic arrays which are bonded to each other by cohesive forces.

Metals occur in both crystalline and noncrystalline forms. The picture of a metallic crystal is that there are localised ions on lattice sites, with nearly free electrons filling rest of the space. By ion we mean a nucleus plus the closed-shell electrons, that is, those electrons which are essentially unchanged when the atoms are brought together to form a solid. The nearly free electrons are the valence electrons which are outside the last closed shell of each ion.

Generally speaking, a crystal is spatially inhomogeneous at a microscopic level. Their spatially ordered structure generates a specific microstructure of the average field $\mathbf{E}$ and gives rise to a difference between the local fields and their value averaged over the unit cell. However, the response function will be very complicated and almost hopeless to evaluate under such a circumstance. In the work through the thesis, spatial homogeneity is assumed. In this case, the response function depends only on the difference between the space and the time arguments $(\mathbf{r}' - \mathbf{r}, t' - t)$.

1.5 Basic Hamiltonian

The basic Hamiltonian which describes our model of the solid with an external test charge is of the form

$$H = H_{ion} + H_{el} + H_{ion-el} + H_{ext}, \tag{1.5}$$

where

$$H_{ion} = \sum_i \frac{P_i^2}{2M} + \frac{1}{2}\sum_{i\neq j} V(\mathbf{R}_i - \mathbf{R}_j), \tag{1.6}$$

$$H_{el} = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \tag{1.7}$$

$$H_{ion-el} = \sum_{i,j} V(\mathbf{r}_i - \mathbf{R}_j). \tag{1.8}$$

H_{ion} describes a collection of ions which interact through a pair potential $V(\mathbf{R}_i - \mathbf{R}_j)$ which depends only on the distance between the ions. H_{el} describes the valence (free) electrons (the electrons outside the last closed shell), which are assumed to interact via Coulomb interaction. H_{el-ion} describes the interaction between the electrons and ions, which is assumed to be represented by a suitably chosen potential which will be discussed in chapter 4. H_{ext} is the interaction between external charge and ions and electrons. The form of it will be presented in the next chapter.

Here a number of approximations have been made in the treatment of the solid. We assume that the interaction between ions depends on the distance between the ions only; but it is not correct when the coupling between the closed-shell electrons on different ions begins to play an important role. We will neglect the fact where the Pauli principle plays an important role in the interaction between the valence electrons and core electrons, and that the interaction may no longer be represented by a simple local potential. It is desirable to consider the validity of these approximations in detail, but a detailed study of these approximations lies beyond the scope of this thesis.

1.6 Scope of the thesis

As is clear from the title, we shall focus our attention on the dielectric function of metals and alloys in crystalline form. Although some of the treatments presented in the thesis will be comparatively general, for the most part the specific applications which are developed in the course of the thesis have to do with "simple" crystal structure and models such as the essentially free-electron-like behaviour of conduction electrons in "simple" metals. It has to be emphasized that it is not possible to obtain exact solutions. There are simply too many variables and too many approximations that one is forced to make along the way.

The method of evaluating the dielectric function of a metal is based on imposing the external field due to a test charge, and evaluating the induced polarisation and the resulting induced field due to the response of the electrons and ions. This approach with variations has been followed for a long time. Chapter 2 is started by introducing two test point charges in a system. In free space, the two point charges interact through the Coulomb potential. When free space is replaced by a medium, their interaction is screened. The screening property of the medium is an important subject in condensed matter physics. The dielectric function can be calculated by various methods: for example, by calculating directly the correlator $< \delta\rho_{in}(x), \delta\rho_{in}(x') >$, or by writing the equations of motion for electrons and ions, or by the method of the self-consistent description of an inhomogeneous electron-ion system. Such calculations have been performed in a large number of works [see, for example, the reviews by Hedin and Lundqvist (1969), Pick (1970), Maksimov and Khomskii (1982), Dolgov and Maksimov (1989)]. I am following a simple model which gives the dielectric function directly from the equations of motion of the electrons and ions, and also it enables us to relate the result to a multicomponent plasma model of the metal. In a later chapter, the concept of local-field correction $G(\mathbf{k}, \omega)$ is introduced into the calculation of electronic dielectric function. The results are shown in figures in which can be seen that the local-field correction plays a crucial role in the work. The correction from the van der Waals interaction between the ions are evaluated.

In Chapter 3, following the approach in the proceeding chapter, an alloy is

explored from a somewhat more general point of view.

Pseudopotential is introduced in Chapter 4. The fundamental theory of pseudopotential will not be discussed in this chapter but the comparison will be made of the results of dielectric function based on earlier work on the pseudopotential. As mentioned, in using approximate methods for calculating dielectric function, it will be seen that the accuracy of the results will depend upon the particular choice of pseudopotential. As an application of the dielectric function evaluated in this thesis, the superconducting energy gap is evaluated in a few cases. It is not possible to achieve realistic value for the energy gap relative to its predicted value of BCS theory by the method followed in this thesis. This is because of the fact that I have not found the suitable values of the parameters (mainly in the electronic dielectric function and in the pseudopotential) that enter this theory. However, inclusion of van der Waals interaction improve the energy gap in the right direction by about 6.8% from the calculated value for aluminium and 4.9% for the binary alloy NbTa.

CHAPTER 2

Dielectric Function of Metals

The total dielectric response of a solid has contributions from the polarisability of the electrons, and that associated with ionic displacements. In this chapter, a method for evaluating the dielectric response of simple metals is developed. Using the dielectric function of the electron gas in which a local-field is considered and the equation of motion of ions, the explicit form of the total dielectric function is obtained. Features and applications of this method are discussed taking the example of aluminium. In the example, the corrections from van der Waals interaction are evaluated and shown in the figures.

2.1 The equation of motion of charge fluctuations

This model starts by considering simple metals which are assumed to have the simplest crystal structure, with similar ions and equal spacing. One of the first things to consider is a time-dependent response of the electron-ion system to a weak external test charge density which varies in space and time. In such a simple metal, represented by a monatomic lattice with N sites, it can be assumed that the equilibrium position of ions are at the lattice points $\{\mathbf{R}_{io}\}$, and the free electrons have the equilibrium density n_o. The corresponding quantities for the perturbed system are $\mathbf{R}_i = \mathbf{R}_{io} + \mathbf{u}_i$ and $n_e(\mathbf{r}, t) = n_o + n(\mathbf{r}, t)$. Here $\mathbf{R}_i$ is the instantaneous position of the ith ion, $\mathbf{u}_i$ is the displacement from $\mathbf{R}_{io}$, $n(\mathbf{r}, t)$ is the induced electron density and $n_e(\mathbf{r}, t)$ is the total electron density. The interaction between every pair of ions is specified by $V(\mathbf{R}_i - \mathbf{R}_j)$ and the interaction between the test charge and the ions is taken as Coulombic. The Hamiltonian for the ionic system

in the presence of an external test charge density $\rho_{ext}(\mathbf{r},t)$ is then given by

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2M} + \frac{1}{2}\sum_{i\neq j}^{N} V(\mathbf{R}_i - \mathbf{R}_j) - Ze^2 \sum_{i=1}^{N} \int_\Omega n_e(\mathbf{r},t) V^{ie}(\mathbf{r}-\mathbf{R}_i) d^3r$$

$$+ Ze \sum_{i=1}^{N} \int_\Omega \frac{\rho_{ext}(\mathbf{r},t)}{|\mathbf{R}_i - \mathbf{r}|} d^3r. \tag{2.1}$$

where $\mathbf{P}_i$ is the momentum of the ith ion with mass M, and (Ze) is its charge. N is the total number of ions in the system of volume Ω. $V^{ie}(\mathbf{r}-\mathbf{R}_i)$ is the interaction potential between an ion at position $\mathbf{R}_i$ and a conduct electron at $\mathbf{r}$. The form of $V^{ie}(\mathbf{r}-\mathbf{R}_i)$ including pseudopotential will be discussed later.

Assume $\mathbf{u}_i$ is small so that one can expand any quantity involving $\mathbf{R}_i$ as a Taylor series in $\mathbf{u}_i$. Thus one expands $V(\mathbf{R}_i - \mathbf{R}_j)$ about the equilibrium separation $\mathbf{R}_{io} - \mathbf{R}_{jo}$, retaining up to the quadratic terms in $\mathbf{u}_i$, giving

$$\sum_{i\neq j} V(\mathbf{R}_i - \mathbf{R}_j) = \sum_{i\neq j} \{V(\mathbf{R}_{io} - \mathbf{R}_{jo}) + [(\mathbf{u}_i \cdot \nabla_i)(\mathbf{u}_i \cdot \nabla_i)$$

$$+ (\mathbf{u}_i \cdot \nabla_i)(\mathbf{u}_j \cdot \nabla_j)] V(\mathbf{R}_{io} - \mathbf{R}_{jo}\}. \tag{2.2}$$

The terms linear in $\mathbf{u}_i$ do not contribute because of the equilibrium condition $\Sigma_j \nabla V(\mathbf{R}_i - \mathbf{R}_j) = 0$ (the force on any atom vanishes in equilibrium). The first term in the right-hand side is a constant and may be neglected. Equation (2.2) is therefore simply

$$\sum_{i\neq j} V(\mathbf{R}_i - \mathbf{R}_j) = constant + \sum_{i,j} \mathbf{u}_i \overleftrightarrow{\mathbf{A}}_{ij} \mathbf{u}_j. \tag{2.3}$$

It will be useful to obtain an explicit expression for $\overleftrightarrow{\mathbf{A}}_{ij}$. Supposing the potential energy term is well behaved, it may be expanded in a Fourier series,

$$V(\mathbf{R}_i - \mathbf{R}_j) = \frac{1}{\Omega} \sum_{\mathbf{k}} V_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{R}_j)}. \tag{2.4}$$

Noting that the summation here is over all values of $\mathbf{k}$, one can then show that the dyadic is given by

$$\overleftrightarrow{\mathbf{A}}_{ij} = \frac{1}{\Omega}\sum_{\mathbf{k}} \mathbf{kk} V_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_{i0}-\mathbf{R}_{j0})} \qquad i \neq j, \tag{2.5}$$

$$\overleftrightarrow{\mathbf{A}}_{ii} = -\frac{1}{\Omega}\sum_{\mathbf{k}}\sum_{j} \mathbf{kk} V_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_{i0}-\mathbf{R}_{j0})} \qquad i \neq j. \tag{2.6}$$

where $V_{\mathbf{k}} = V_{\mathbf{k}}^{c} + V_{\mathbf{k}}^{nc}$. $V_{\mathbf{k}}^{c}$ is the Coulomb part of the interaction given by $4\pi e^2/k^2$, $V_{\mathbf{k}}^{nc}$ is the non-Coulomb part and $V_{\mathbf{k}}$ is the Fourier transform of $V(\mathbf{r})$. Thus the equation of motion for the ith ion will be

$$\frac{\partial \mathbf{P}_i}{\partial t} = -\nabla_i H = M\frac{\partial^2 \mathbf{u}_i}{\partial t^2}. \tag{2.7}$$

where M is the ionic mass, or

$$M\frac{\partial^2 \mathbf{u}_i}{\partial t^2} = [\mathbf{1}] + [\mathbf{2}] + [\mathbf{3}], \tag{2.8}$$

where

$$[\mathbf{1}] = -\sum_{j} \overleftrightarrow{\mathbf{A}}_{ij}\mathbf{u}_j,$$

$$[\mathbf{2}] = Ze^2\nabla_i \sum_{j}\int_{\Omega} n_e(\mathbf{r},t)V^{ie}(\mathbf{r}-\mathbf{R}_j)d^3r,$$

$$[\mathbf{3}] = -Ze\nabla_i \sum_{j}\int_{\Omega} \frac{\rho_{ext}(\mathbf{r},t)}{|\mathbf{r}-\mathbf{R}_j|}d^3r.$$

2.2 The response function $\chi_e(\mathbf{k},\omega)$

The induced charge density due to a small displacement of the ions, treating the ions as point charges, is

$$\rho_{ion}(\mathbf{r},t) = Ze\sum_{i}[\delta(\mathbf{r}-\mathbf{R}_{io}-\mathbf{u}_i) - \delta(\mathbf{r}-\mathbf{R}_{io})]. \tag{2.9}$$

Since the external test charge density $\rho_{ext}(\mathbf{r},t)$ is assumed to be small, a response function $\chi_e(\mathbf{r},\mathbf{r}',t,t')$ of the electron system to an external charge and ion displacement is introduced. As mentioned in the first chapter, a crystal is spatially inhomogeneous at a microscopic level. But then the response function will be very complicated and it would be difficult to evaluate anything under such a circumstance. In this case, a spatial homogeneity is assumed. Therefore the response function $\chi_e(\mathbf{r},\mathbf{r}',t,t')$ depends only on the difference in both space and time which can be written as $\chi_e(\mathbf{r}-\mathbf{r}',t-t')$ and may be described in the form,

$$-en(\mathbf{r},t) = \int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')[\rho_{ext}(\mathbf{r}',t') + \rho_{ion}(\mathbf{r}',t')]d^3r'dt'. \quad (2.10)$$

In reciprocal space, it has the form

$$-en(\mathbf{k},\omega) = \chi_e(\mathbf{k},\omega)[\rho_{ext}(\mathbf{k},\omega) + \rho_{ion}(\mathbf{k},\omega)]. \quad (2.11)$$

where

$$\chi_e(\mathbf{k},\omega) = \frac{1}{\varepsilon_e(\mathbf{k},\omega)} - 1. \quad (2.12)$$

This follows from the procedure of Gorobchenko *et al* (1989). Here $\varepsilon_e(\mathbf{k},\omega)$ is the electronic dielectric function. The process to get the particular relation between $\chi_e(\mathbf{k},\omega)$ and $\varepsilon_e(\mathbf{k},\omega)$ is shown in Appendix B. The electronic dielectric function used here does not take into account interband electronic transition and hence it is basically that of a one-band model.

2.3 Total dielectric function of the electron-ion system

Using the Fourier relations between $\mathbf{u}$ and $\mathbf{q}$ (refer to Appendix A), the left hand side of equation (2.8) becomes

$$M\frac{\partial^2\mathbf{u}_i}{\partial t^2} = \frac{M}{N}\sum_{\mathbf{k}\in\mathbf{K}} \ddot{\mathbf{q}}_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{R}_i}, \quad (2.13)$$

and the first term on the right hand side of equation (2.8) with the expansion (2.5) and (2.6) becomes

$$[\mathbf{1}] = -\frac{1}{\Omega}\sum_{j,\mathbf{k}} \mathbf{k}\mathbf{k}V_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\mathbf{u}_j + \frac{1}{\Omega}\sum_{j,\mathbf{k}} \mathbf{k}\mathbf{k}V_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\mathbf{u}_i. \tag{2.14}$$

where $\mathbf{k}$ runs over all possible values. Since the two sums cancel when $i = j$, the restriction $i \neq j$ has been removed. Equation (2.14) may therefore be written as,

$$\begin{aligned} -\sum_j \overleftrightarrow{\mathbf{A}}_{ij}\mathbf{u}_j &= -\frac{1}{\Omega N}\sum_{j,\mathbf{k},\mathbf{k}'\in\mathbf{K}} \mathbf{k}\mathbf{k}V_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\mathbf{q}_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{R}_j} \\ &+\frac{1}{\Omega N}\sum_{j,\mathbf{k},\mathbf{k}'\in\mathbf{K}} \mathbf{k}\mathbf{k}V_{\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_i-\mathbf{R}_j)}\mathbf{q}_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{R}_i} \\ = \; -\frac{1}{\Omega}\sum_m \sum_{\mathbf{k}'\in\mathbf{K}} &[(\mathbf{k}'+\mathbf{K}_m)(\mathbf{k}'+\mathbf{K}_m)V_{\mathbf{k}'+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m V_{\mathbf{K}_m}]e^{i\mathbf{k}'\cdot\mathbf{R}_i}\mathbf{q}_{\mathbf{k}'}, \end{aligned} \tag{2.15}$$

where the summation over j has been carried out, and the sum over $\mathbf{k}$ has been reduced to a sum over m using equation (A.9) in Appendix A.

Considering now the second term on the right hand side of equation (2.8), the electron density may be expanded as

$$n_e(\mathbf{r},t) = n_o + n(\mathbf{r},t)$$

$$= n_o - \frac{1}{e}\int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')[\rho_{ext}(\mathbf{r}',t') + \rho_{ion}(\mathbf{r}',t')]d^3r'dt'$$

$$= n_o - Z\int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')\sum_i[\delta(\mathbf{r}'-\mathbf{R}_i) - \delta(\mathbf{r}'-\mathbf{R}_{io})]d^3r'dt'$$

$$-\frac{1}{e}\int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t)d^3r'dt'$$

$$= -Z\sum_i \chi_e(\mathbf{r}-\mathbf{R}_i,t) - \frac{1}{e}\int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t)d^3r'dt'. \tag{2.16}$$

Therefore the second term is

$$[\mathbf{2}] = Ze^2\nabla_i \sum_j \int_\Omega [-Z \sum_i \chi_e(\mathbf{r}-\mathbf{R}_i,t)$$

$$-\frac{1}{e}\int_{\Omega,t'} \chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t)d^3r'dt']V^{ie}(\mathbf{r}-\mathbf{R}_j)d^3r$$

$$= [\mathbf{2.a}] + [\mathbf{2.b}], \tag{2.17}$$

where

$$[\mathbf{2.a}] = -Z^2e^2\nabla_i \sum_{\ell j} \int_\Omega \chi_e(\mathbf{r}-\mathbf{R}_\ell,t)V^{ie}(\mathbf{r}-\mathbf{R}_j)d^3r,$$

$$[\mathbf{2.b}] = -Ze\nabla_i \sum_j \int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t)V^{ie}(\mathbf{r}-\mathbf{R}_j)d^3r'd^3rdt'.$$

As shown in Appendices A and B

$$[\mathbf{2.a}] = -\frac{Z^2e^2}{2\Omega^2}\nabla_i \sum_{lj}\int_\Omega \sum_{\mathbf{k},\mathbf{k}'} \chi_e(\mathbf{k},t)e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_l)}V^{ie}_{\mathbf{k}'}e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{R}_j)}d^3r$$

$$= -\frac{Z^2e^2}{2\Omega}\nabla_i \sum_{lj}\sum_{\mathbf{k}}\int_{-\infty}^{\infty} \chi_e(\mathbf{k},t)V^{ie}_{\mathbf{k}'}e^{-i\mathbf{k}\cdot(\mathbf{R}_j-\mathbf{R}_l)}$$

$$= -\frac{Z^2e^2}{2\Omega}\nabla_i \sum_{lj,\mathbf{k}} \chi_e(\mathbf{k},t)V^{ie}_{\mathbf{k}'}e^{-i\mathbf{k}\cdot(\mathbf{R}_{jo}-\mathbf{R}_{lo})}[1+(i\mathbf{k}\cdot\mathbf{u}_j - i\mathbf{k}\cdot\mathbf{u}_l)$$

$$-(\mathbf{k}\cdot\mathbf{u}_j)(\mathbf{k}\cdot\mathbf{u}_j)+(\mathbf{k}\cdot\mathbf{u}_j)(\mathbf{k}\cdot\mathbf{u}_l)].$$

retaining up to quadratic terms in $\mathbf{u}_i$. The first term is constant and may be neglected. The second term, linear in $\mathbf{u}_i$, will bring no contribution, as can be easily shown using the symmetry of the system. So it can be written as,

$$[\mathbf{2.a}] = -\frac{Z^2e^2}{\Omega}\sum_{l,\mathbf{k}}\chi_e(\mathbf{k},t)V^{ie}_{\mathbf{k}'}e^{-i\mathbf{k}\cdot(\mathbf{R}_{jo}-\mathbf{R}_{lo})}[-\mathbf{k}\mathbf{k}\cdot\mathbf{u}_i+\mathbf{k}\mathbf{k}\cdot\mathbf{u}_l]$$

$$= -\frac{Z^2e^2}{\Omega N}\sum_{l,\mathbf{k}}\chi_e(\mathbf{k},t)V^{ie}_{\mathbf{k}'}e^{-i\mathbf{k}\cdot(\mathbf{R}_{io}-\mathbf{R}_{lo})}\sum_{\mathbf{k}'\in\mathbf{K}}[-\mathbf{k}\mathbf{k}\cdot\mathbf{q}_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{R}_i}+\mathbf{k}\mathbf{k}\cdot\mathbf{q}_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{R}_l}].$$

Here $\mathbf{q}_{\mathbf{k}}$ is the normal coordinate. Summing over l,

$$[\mathbf{2.a}] = -\frac{Z^2e^2}{\Omega}\sum_{m}\sum_{\mathbf{k}'\in\mathbf{K}}[-\mathbf{K}_m\mathbf{K}_m\chi_e(\mathbf{K}_m,t)V^{ie}_{\mathbf{K}_m}$$

$$+(\mathbf{k}'+\mathbf{K}_m)(\mathbf{k}'+\mathbf{K}_m)\chi_e(\mathbf{k}'+\mathbf{K}_m,t)V^{ie}_{\mathbf{k}'+\mathbf{K}_m}]\cdot\mathbf{q}_{\mathbf{k}'}e^{i\mathbf{k}'\cdot\mathbf{R}_i}. \qquad (2.18)$$

Referring to Appendix B the term $[\mathbf{2.b}]$ is

$$\begin{aligned}[\mathbf{2.b}] &= -\frac{Ze}{\Omega}\nabla_i\sum_{j,\mathbf{k}}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},t-t')\rho_{ext}(\mathbf{k},t')V^{ie}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}_j}dt' \\ &\approx -\frac{iZe}{2\pi\Omega}\sum_{\mathbf{k}}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)\rho_{ext}(\mathbf{k},\omega)\mathbf{k}V^{ie}_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}_i}e^{i\omega t}d\omega \qquad (2.19)\end{aligned}$$

The approximation is taken by truncating the series after the first order term in $e^{i\mathbf{k}\cdot\mathbf{R}_i}$. The last term of equation (2.8) is given by

$$\begin{aligned}[\mathbf{3}] &= -\frac{4\pi Ze}{\Omega^2}\nabla_i\sum_{j}\int_{\Omega}\sum_{\mathbf{k},\mathbf{k}'}\rho_{ext}(\mathbf{k},t)\frac{1}{k'^2}e^{i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{R}_j)}d^3r \\ &= -\frac{4\pi Ze}{\Omega^2}\nabla_i\sum_{j,\mathbf{k}}\rho_{ext}(\mathbf{k},t)\frac{1}{k^2}e^{i\mathbf{k}\cdot\mathbf{R}_j} \\ &\approx -\frac{i4\pi Ze}{\Omega^2}\sum_{\mathbf{k}}\rho_{ext}(\mathbf{k},t)\frac{\mathbf{k}}{k^2}e^{i\mathbf{k}\cdot\mathbf{R}_i}. \qquad (2.20)\end{aligned}$$

The external test charge is assumed to have the following form in space and time,

$$\rho_{ext}(\mathbf{r},t) = \frac{1}{\Omega}\rho_{ext}(\mathbf{k}_o,\omega_o)e^{i\mathbf{k}_o\cdot\mathbf{r}-i\omega_o t}. \tag{2.21}$$

In reciprocal space, referring to Appendix B, equation (2.8) can be written in the form (with all the notations explained above),

$$-M\ddot{\mathbf{q}}_\mathbf{k} + N\{\sum_m(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W_{\mathbf{k}+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m W_{\mathbf{K}_m}\}\cdot\mathbf{q}_\mathbf{k}$$

$$= -\frac{iM\omega_I^2\rho_{ext}(\mathbf{k},\omega_o)\mathbf{k}}{Ze\varepsilon_e(\mathbf{k},\omega_o)k^2}, \tag{2.22}$$

where

$$\begin{aligned} W_\mathbf{k} &= V_\mathbf{k}^{nc} + V_\mathbf{k}^{c} + (\frac{1}{\varepsilon_e(\mathbf{k},\omega_o)} - 1)V_\mathbf{k}^{ie} \\ \omega_I^2 &= \frac{4\pi(Ze)^2N}{MV} \\ \mathbf{q}_\mathbf{k} &\equiv \sum_j \mathbf{u}_j e^{-i\mathbf{k}\cdot\mathbf{R}_{jo}}. \end{aligned}$$

If considering the contribution to the induced charge only from the induced polarisation associated with ionic displacements from their equilibrium positions, the total induced charge density $\rho_{in}(\mathbf{r},t)$ will be

$$\rho_{in}(\mathbf{r},t) = -en(\mathbf{r},t) + \rho_{ion}(\mathbf{r},t). \tag{2.23}$$

Its form in reciprocal space is

$$\rho_{in}(\mathbf{k},\omega) = -en(\mathbf{k},\omega) + \rho_{ion}(\mathbf{k},\omega). \tag{2.24}$$

Using equation (2.11), (2.9) and (2.21) in (2.24), a brief calculation leads to

$$\rho_{in}(\mathbf{k}_o,\omega_o) = (\frac{1}{\varepsilon_e(\mathbf{k}_o,\omega_o)} - 1)\rho_{ext}(\mathbf{k}_o,\omega_o) - \frac{iZe\mathbf{k}\cdot\mathbf{q}_\mathbf{k}}{\varepsilon_e(\mathbf{k}_o,\omega_o)}. \tag{2.25}$$

By solving the equation (2.22), we get

$$\mathbf{q}_\mathbf{k} = -\frac{i\rho_{ext}(\mathbf{k},\omega_o)\delta_{\mathbf{k}\mathbf{k}_o}}{Ze\varepsilon_e(\mathbf{k},\omega_o)k^2}\overleftrightarrow{\mathbf{\Phi}}^{-1}\cdot\mathbf{k} \tag{2.26}$$

where $\overleftrightarrow{\mathbf{\Phi}}$ is the dynamic matrix and has the form

$$\overleftrightarrow{\mathbf{\Phi}}(\mathbf{k},\omega_o) = \frac{1}{\omega_I^2}[\frac{N}{M}\sum_m(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W_{\mathbf{k}+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m W_{\mathbf{K}_m} - \omega_o^2\overleftrightarrow{\mathbf{I}}]. \tag{2.27}$$

Hence,

$$\rho_{in}(\mathbf{k}_o,\omega_o) = (\frac{1}{\varepsilon_e(\mathbf{k}_o,\omega_o)} - 1)\rho_{ext}(\mathbf{k}_o,\omega_o) - \frac{\rho_{ext}(\mathbf{k}_o,\omega_o)}{\varepsilon_e^2(\mathbf{k}_o,\omega_o)}\frac{\mathbf{k}_o\cdot\overleftrightarrow{\mathbf{\Phi}}^{-1}\cdot\mathbf{k}_o}{k_o^2}. \tag{2.28}$$

The definition of the inverse of the total longitudinal dielectric function $\varepsilon_t(\mathbf{k},\omega)$ is

$$\frac{1}{\varepsilon_t(\mathbf{k},\omega)} = 1 + \frac{\rho_{in}(\mathbf{k},\omega)}{\rho_{ext}(\mathbf{k},\omega)}. \tag{2.29}$$

Thus we finally get the explicit form for the inverse of the total dielectric function as the following,

$$\frac{1}{\varepsilon_t(\mathbf{k}_o,\omega_o)} = \frac{1}{\varepsilon_e(\mathbf{k}_o,\omega_o)} - \frac{1}{\varepsilon_e^2(\mathbf{k}_o,\omega_o)}\frac{\mathbf{k}_o\cdot\overleftrightarrow{\mathbf{\Phi}}^{-1}\cdot\mathbf{k}_o}{k_o^2}, \tag{2.30}$$

If ω_o is equal to zero in formula (2.30), then it has the same form as the formula given by Dolgov and Maksimov [see Dolgov and Maksimov (1989)] for the static dielectric function.

As an example of the use of the above formula (2.30), we will discuss the dispersion relation for longitudinal charge oscillation modes in a metal at long wave lengths. The electronic dielectric function at long wave lengths can be obtained

from the hydrodynamic model of the electron gas [see Mahanty and Das (1989)] (and also from RPA),

$$\frac{1}{\varepsilon_e(\mathbf{k},\omega)} = 1 - \frac{\omega_p^2}{\omega_p^2 + \beta_e^2 k^2 - \omega^2}, \tag{2.31}$$

where β_e^2 is proportional to the square of the Fermi velocity [see Mahanty and Das (1989)], and hence $\beta_e^2 > 0$.

In the small $\mathbf{k}$ region,

$$\overleftrightarrow{\Phi}(\mathbf{k},\omega) \approx \frac{1}{\omega_I^2}[\frac{N}{M}\mathbf{k}\mathbf{k}W_{\mathbf{k}} - \omega^2\overleftrightarrow{\mathbf{I}}],$$

thus

$$\mathbf{k}\cdot\overleftrightarrow{\Phi}^{-1}\cdot\mathbf{k} = \frac{k^2\omega_I^2}{\frac{N}{M}W_{\mathbf{k}}k^2 - \omega^2}.$$

Assuming that the ion plasma frequency (in absence of interaction with electrons) has the form

$$\omega_I^2(\mathbf{k}) = \omega_I^2 + \beta_I^2 k^2, \tag{2.32}$$

when

$$\frac{N}{M}W_{\mathbf{k}}k^2 = \frac{\omega_I^2}{\varepsilon_e(\mathbf{k},\omega)} + \beta_I^2 k^2, \tag{2.33}$$

we get the following expression for total dielectric function

$$\varepsilon_t(\mathbf{k},\omega) = 1 - \frac{\omega_e^2}{\omega^2 - \beta_e^2 k^2} - \frac{\omega_I^2}{\omega^2 - \beta_I^2 k^2}. \tag{2.34}$$

Equations (2.33) and (2.34) are equivalent to the assumption [see Montgomery (1971)] that the plasma frequency of the ions in the absence of any response of the electrons is $\omega_I^2(\mathbf{k}) = \omega_I^2 + \beta_I^2 k^2$, and that of the electrons with non-responsive ions is $\omega_e^2(\mathbf{k}) = \omega_e^2 + \beta_e^2 k^2$. The dispersion parameter β_I^2 of the ion plasma branch is governed by the Coulombic and non-Coulombic interaction between ions, and will be discussed in detail later.

If we set $\varepsilon(\mathbf{k},\omega) = 0$, the dispersion relations for small wave vector $\mathbf{k}$ [see Mahanty and Das (1989)] are:

$$\omega_P^2 \simeq \frac{1}{2}[\omega_p^2 + \beta_e^2 k^2 + \omega_I^2 + \beta_I^2 k^2 + \sqrt{(\omega_p^2 + \beta_e^2 k^2 - \omega_I^2 - \beta_I^2 k^2)^2 + 4\omega_I^2 \omega_p^2}]$$

$$\simeq \omega_p^2 + \omega_I^2 + \frac{\omega_p^2 \beta_e^2 + \omega_I^2 \beta_I^2}{\omega_p^2 + \omega_I^2} k^2; \tag{2.35}$$

$$\omega_A^2 \simeq \frac{1}{2}[\omega_p^2 + \beta_e^2 k^2 + \omega_I^2 + \beta_I^2 k^2 - \sqrt{(\omega_p^2 + \beta_e^2 k^2 - \omega_I^2 - \beta_I^2 k^2)^2 + 4\omega_I^2 \omega_p^2}]$$

$$\simeq \frac{\omega_p^2 \beta_I^2 + \omega_I^2 \beta_e^2}{\omega_p^2 + \omega_I^2} k^2. \tag{2.36}$$

The longitudinal dispersion relations can be found directly from equation (2.22). The way to achieve this is simply to find the roots of the equation. For long wave lengths, it has the form

$$\ddot{\mathbf{q}}_\mathbf{k} + \frac{N}{M} W_\mathbf{k} \mathbf{k}\mathbf{k} \cdot \mathbf{q}_\mathbf{k} = 0. \tag{2.37}$$

We can then get the longitudinal dispersion relations through the equation of motion of $\mathbf{k} \cdot \mathbf{q}_\mathbf{k}$,

$$\mathbf{k} \cdot \ddot{\mathbf{q}}_\mathbf{k} + \frac{N}{M} W_\mathbf{k} k^2 \mathbf{k} \cdot \mathbf{q}_\mathbf{k} = 0 \tag{2.38}$$

Assuming the time dependence of $\mathbf{k} \cdot \mathbf{q}_\mathbf{k} \propto e^{i\omega t}$, we get

$$-\omega^2 + \frac{N}{M} W_\mathbf{k} k^2 = 0. \tag{2.39}$$

Again, taking

$$\frac{N}{M} W_\mathbf{k} k^2 = \frac{\omega_I^2}{\varepsilon_e(\mathbf{k},\omega)} + \beta_I^2 k^2 \tag{2.40}$$

as before, and using (2.31), the solutions of (2.39) are obtained in the form,

$$\omega_1^2 \simeq \frac{1}{2}[\omega_p^2 + \beta_e^2 k^2 + \omega_I^2 + \beta_I^2 k^2 + \sqrt{(\omega_p^2 + \beta_e^2 k^2 - \omega_I^2 - \beta_I^2 k^2)^2 + 4\omega_I^2 \omega_p^2}]$$

$$\simeq \omega_p^2 + \omega_I^2 + \frac{\omega_p^2\beta_e^2 + \omega_I^2\beta_I^2}{\omega_p^2 + \omega_I^2}k^2; \tag{2.41}$$

$$\omega_2^2 \simeq \frac{1}{2}[\omega_p^2 + \beta_e^2k^2 + \omega_I^2 + \beta_I^2k^2 - \sqrt{(\omega_p^2 + \beta_e^2k^2 - \omega_I^2 - \beta_I^2k^2)^2 + 4\omega_I^2\omega_p^2}]$$

$$\simeq \frac{\omega_p^2\beta_I^2 + \omega_I^2\beta_e^2}{\omega_p^2 + \omega_I^2}k^2. \tag{2.42}$$

Thus we get the same results as (2.35) and (2.36).

2.4 The contribution from van der Waals interaction

We can take equation (2.34) as a simple example, to explore how and where $\varepsilon_t(\mathbf{k}, 0)$ can be negative. In this model since β_e^2 is positive, the only possibility for the total static dielectric function to be negative for small $\mathbf{k}$ is if β_I^2 is negative. In fact, β_I^2 is already known to be negative in a Coulomb lattice [see Pines (1963)]. The non-Coulomb interaction between ions can accentuate this effect. The dominant non-Coulomb interaction is the attractive van der Waals interaction, the strength of which is determined by the polarisability of the ions [see Maggs and Ashcroft (1987), Mahanty and Taylor (1978) and Rehr *at al* (1975)].

We take a model which consists of point ions located on a lattice, which is embedded in a uniform non-responsive background of electrons. The equation of motion of the jth ion has the form

$$M\ddot{\mathbf{u}}_j = -\nabla_j \sum_i V^c(\mathbf{R}_i - \mathbf{R}_j) - \nabla_j \sum_i V^{nc}(\mathbf{R}_i - \mathbf{R}_j), \qquad i \neq j. \tag{2.43}$$

V^{nc} is van der Waals interaction and has the form: [see Mahanty and Taylor (1978)]

$$V^{nc}(r) \approx -\frac{1}{r^6}\frac{3\hbar}{\pi}\int_0^\infty \frac{d\xi\xi^4\alpha_1(i\xi)\alpha_2(i\xi)}{(\omega_p^2 + \xi^2)^2}, \tag{2.44}$$

where $\alpha_j(\omega)$ is the polarisability at the frequency ω of the jth ion. It can be assumed

to have the form [see Mahanty and Taylor (1978)], $\alpha_j(\omega) = e^2 n_j / m_e(\omega_j^2 - \omega^2)$ where ω_j is the principal electronic absorption frequency. Equation (2.43) becomes

$$\overleftrightarrow{\Phi}(\mathbf{k},\omega)\begin{pmatrix} q_{\mathbf{k}_{(x)}} \\ q_{\mathbf{k}_{(y)}} \\ q_{\mathbf{k}_{(z)}} \end{pmatrix} = 0, \tag{2.45}$$

where $\overleftrightarrow{\Phi}$ is the dynamic matrix in the uniform background model. It has the form

$$\overleftrightarrow{\Phi}(\mathbf{k},\omega) = \frac{1}{\omega_I^2}[\frac{N}{M}\sum_m(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)V_{\mathbf{k}+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m V_{\mathbf{K}_m} - \omega^2\overleftrightarrow{\mathbf{I}}]. \tag{2.46}$$

The elements of $\overleftrightarrow{\Phi}$ are evaluated following the procedure of Clark, [see Clark (1958)] and have the following form for a face-centred-cubic lattice of aluminium.

$$\begin{aligned}
\Phi_{11} = {} & -\lambda^2 + S_{11} + \sum_m{}'\{[F(\mathbf{K}_m+\mathbf{k})](K_{mx}+k_x)^2 - F(\mathbf{K}_m)K_{mx}^2\} \\
& + \frac{1}{4\pi}\sum_l\{G_l(\frac{6l_x^2}{l^2} - 2) + H_l[(\frac{3}{l^2} + \frac{a^2\eta}{2})l_x^2 - 1]\} \\
& \times[1 - \cos(\pi k_x l_x)\cos(\pi k_y l_y)\cos(\pi k_z l_z)] \\
& - A\{1152\,[2 - \cos(\pi k_x)\,(\cos(\pi k_y) + \cos(\pi k_z))] \\
& - 384\,(1 - \cos(\pi k_y)\cos(\pi k_z)) \\
& + 84\,(1 - \cos(2\pi k_x)) - 12\,(2 - \cos(2\pi k_y) - \cos(2\pi k_z))\}\,,
\end{aligned} \tag{2.47a}$$

$$\begin{aligned}
\Phi_{12} = {} & S_{12} + \sum_m{}'[F(\mathbf{K}_m+\mathbf{k})](K_{mx}+k_x)(K_{my}+k_y) \\
& + \frac{1}{4\pi}\sum_l[G_l\frac{6l_x l_y}{l^2} + H_l(\frac{3}{l^2} + \frac{a^2\eta}{2})l_x l_y][1 - \cos(\pi k_x l_x)\cos(\pi k_y l_y)\cos(\pi k_z l_z)]
\end{aligned}$$

$$-1536A\sin(\pi k_x)\sin(\pi k_y), \tag{2.47b}$$

where

$$F(x) = \exp(-\pi^2 x^2/a^2\eta)/x^2$$

$$S_{ij} = F(\mathbf{k})k_i k_j$$

$$G_l = [1 - G(\frac{1}{2}\sqrt{\eta}al)]/l^3$$

$$G(x) = (2/\sqrt{\pi})\int_0^x \exp(-z^2)dz$$

$$H_l = (2a\sqrt{\eta}/\sqrt{\pi})\exp(-\frac{1}{4}\eta a^2 l^2)/l^2$$

$$A = \frac{\hbar(\omega_{Al} - 3\omega_p)\alpha_{Al}^2(0)}{64e^2\pi a^5}.$$

The dimensionless 'frequency' λ used here is related to the actual circular frequency ω by $\lambda^2 = \omega^2/\omega_l^2$. The last term in the right-hand side of (2.47a) and (2.47b) arise from the van der Waals interaction. Here the prime denotes the omission of $m = 0$. a is a lattice constant, and η is an arbitrary parameter, the value of which is fixed to achieve rapid convergence of the series in the matrix elements in equation (2.47a) and (2.47b). The subscript l stands for the triad of integers l_x, l_y, l_z which are either all even or one even and two odd, and (h_x, h_y, h_z) are integers which are either all odd or all even. The values of ω_{Al} and $\alpha_{Al}(0)$ are taken from Fraga *et al* (1971).

2.5 Local field correction $G(\mathbf{k})$

In the static situation $\omega_o = 0$, the dielectric function, from equation (2.30), is

$$\frac{1}{\varepsilon_t(\mathbf{k}_o)} = \frac{1}{\varepsilon_e(\mathbf{k}_o)} - \frac{1}{\varepsilon_e^2(\mathbf{k}_o)} \frac{\mathbf{k}_o \cdot \overleftrightarrow{\Phi}^{-1} \cdot \mathbf{k}_o}{k_o^2}, \tag{2.49}$$

When $\mathbf{k}$ is not small, the RPA is a poor approximation and the electronic dielectric function does not have the form 2.31 as indicated in the previous section, A local-field correction was introduced in many approximations which improves electronic dielectric function upon RPA. By considering the local-field correction of the electron system, the electronic dielectric function has a form

$$\varepsilon_e(\mathbf{q},\omega) = 1 - \frac{V(\mathbf{q})\chi_o(\mathbf{q},\omega)}{1 + V(\mathbf{q})\chi_o(\mathbf{q},\omega)G(\mathbf{q},\omega)}. \tag{2.50}$$

The static electronic dielectric function, which is used in all calculations in the thesis, should then be written as

$$\varepsilon_e(\mathbf{k}) = 1 - \frac{V(\mathbf{k})\chi_o(\mathbf{k})}{1 + V(\mathbf{k})\chi_o(\mathbf{k})G(\mathbf{k})}, \tag{2.51}$$

where $\chi_o(\mathbf{k})$ is Lindhard's formula given by:

$$\chi_o(\mathbf{k}) = -\frac{mk_F}{\pi^2\hbar^2}\left[\frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right], \tag{2.52}$$

where k_F is the Fermi wave vector and $x = k/2k_F$. In the following numerical calculation, $G(\mathbf{k})$ is playing a crucial role. Figure 2.1 is a list of results from some of the different theories for the static local-field correction $G(\mathbf{k})$.

In figure 2.1, the dashed line represents Utsumi-Ichimaru theory of static local-field correction. The curve shows that it is slightly greater than 1.0 when q/k_F is near 2.0 [see Gorobchenko *et al* (1989), Utsumi and Ichimaru (1980a,b and 1981a,b) and Iyetoni *at al* (1981)]. The solid line represents Vashishta-Singwi theory of static local-field correction. The curve is going to 0.91 when q/k_F is going to infinity [see Vashishta and Singwi (1972) and Gorobchenko *et al* (1989)]. The long dashed line represents Hubbard-Geldart-Vosko theory of static local-field correction. The

curve is going to 1.0 when q/k_F is going to infinite [see Hubbard (1957), Geldart and Vosko (1966), Pines and Nozieres (1966) and Brovman and Kagan (1974)]

From equation (2.51) and using $G(\mathbf{q})$ from various theories as in figure 2.1, the electronic dielectric function is shown in figure 2.2. Their differences appear between 0.0 - 2.5 of q/k_F.

By substituting the electronic dielectric function from equation (2.51) into equation (2.49), various inverse total dielectric functions are shown in figure 2.3.

The insert shows the variation in the inverse total dielectric function which is clearly negative for most of the region. The results show that the local-field correction $G(\mathbf{q})$ plays a crucial role in determining the value of $\varepsilon_t(\mathbf{q})$. It is expected that a different choice of local field correction may give rise to a different value for the energy gap when $\varepsilon_t(\mathbf{q})$ is used in the BCS gap equation, which will be discussed in Chapter 4. From figure 2.3, all the total dielectric functions have a singularity when $|\mathbf{q}a/2\pi$ goes to 2.0 along (1,0,0) direction. This can be understood by studying longitudinal phonon dispersion of aluminium which starts to increase from 0.0 when $|\mathbf{q}a/2\pi$ starts from 0.0 along (1,0,0) and after a period of 2.0 along(1,0,0) back to 0.0. The 0.0 point at $q/k_o = 2.0$ along (1,0,0) brings in the singularity (see the figure 2.4). The pseudopotential in electron-ion interaction has been considered in figure 2.4, which is similar to the calculations obtained by Brovman and Kagan (1974), this will be discussed in Chapter 4.

It is seen that Hubbard-Geldart-Vosko theory of local-field correction makes the total dielectric function more rapidly negative along (1,0,0), relative to the other local field correction mentioned above.

If the van der Waals correction is added to the inter-ionic potential, it is found to provide some contribution to the negative dielectric function, shown in figure 2.5; this will also be discussed in more detail in Chapter 4.

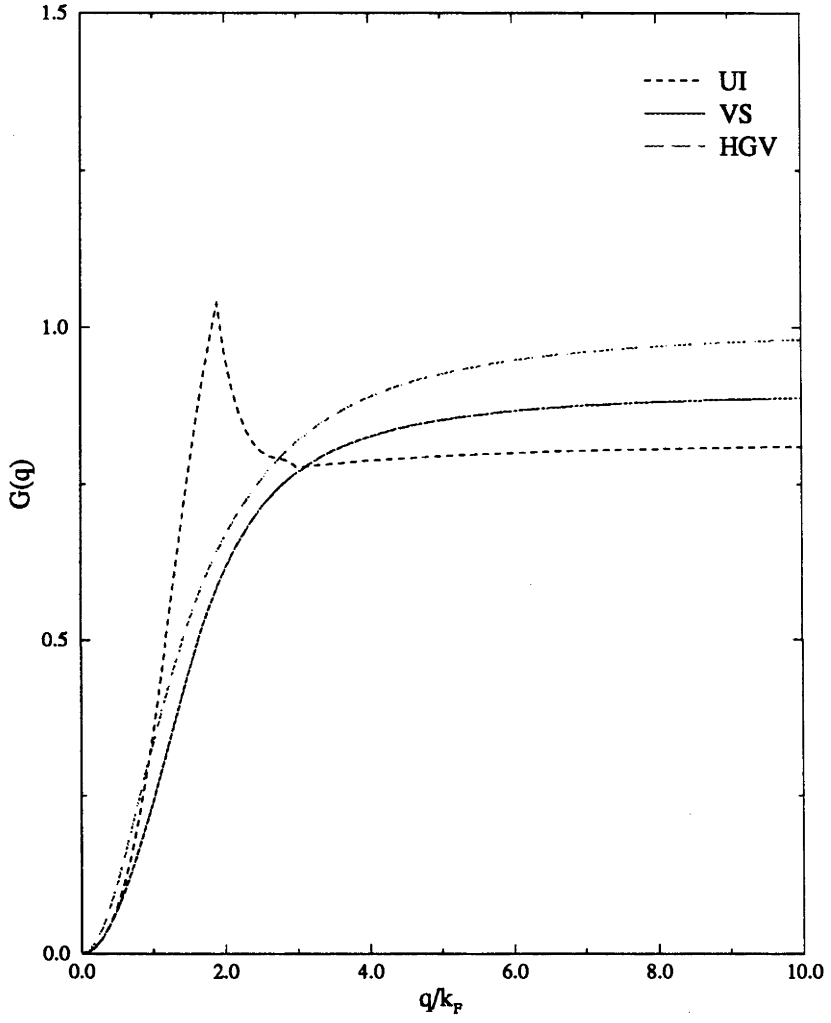

Figure 2.1: Static local-field correction G(**k**) for different theories:
UI – Utsumi-Ichimaru [Gorobchenko (1989)], VS – Vashishta-Singwi [Gorobchenko (1989)] and HGV – Hubbard-Geldart-Vosko [Geldart (1966), Hubbard (1958) and Brovman and Kagan (1974)]

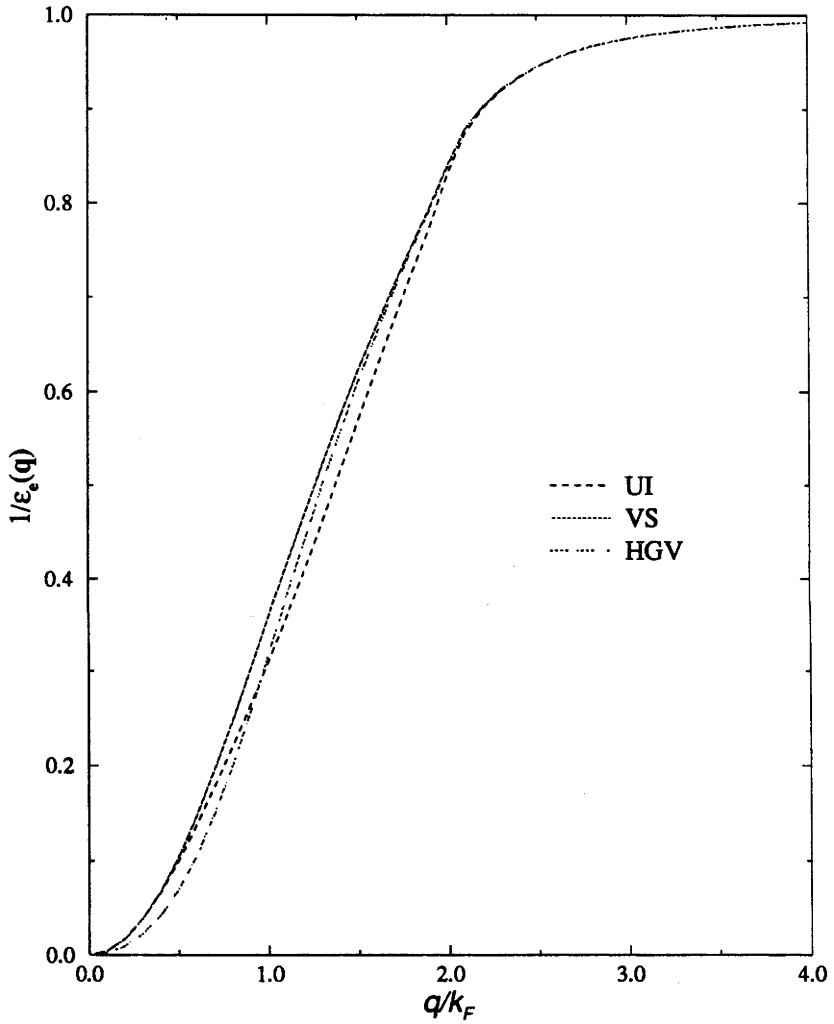

Figure 2.2: Static electronic dielectric function $1/\varepsilon_e(\mathbf{q})$ calculated by using varying local field corrections UI, VS and HGV

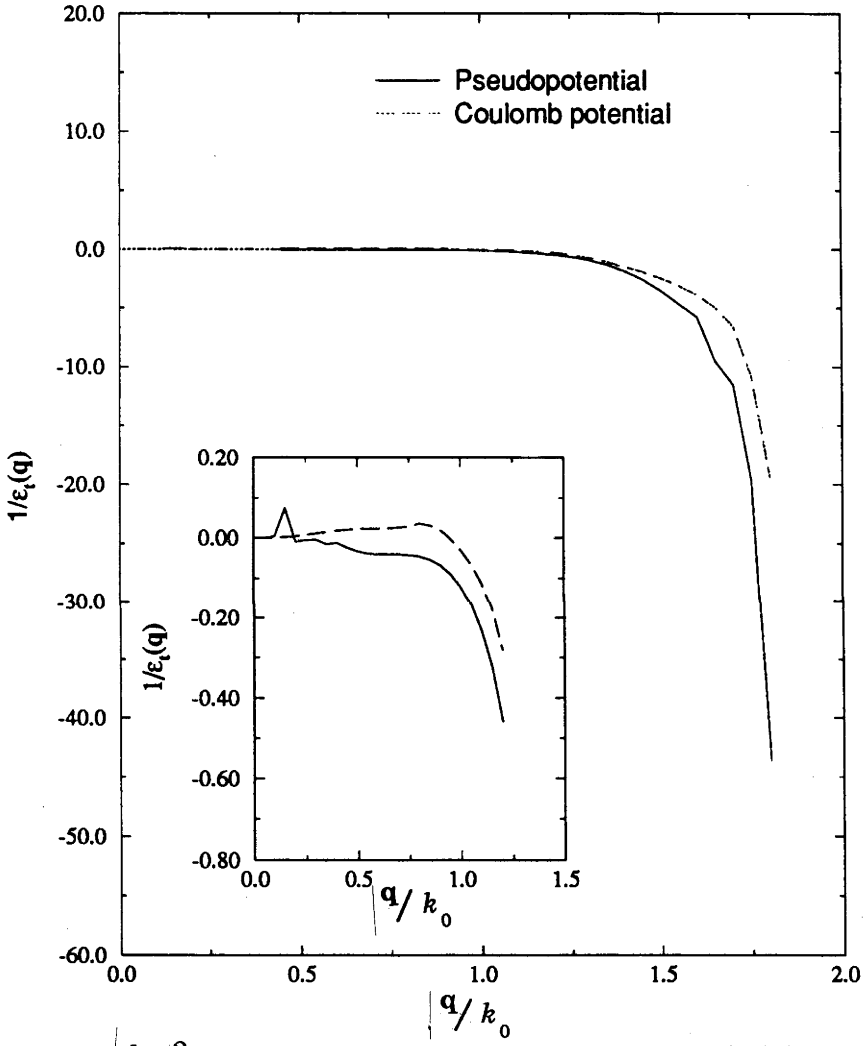

Figure 2.3: $k_0 = 2\pi/a$. The static total dielectric function $1/\varepsilon_t(\mathbf{q})$ along (1,0,0)

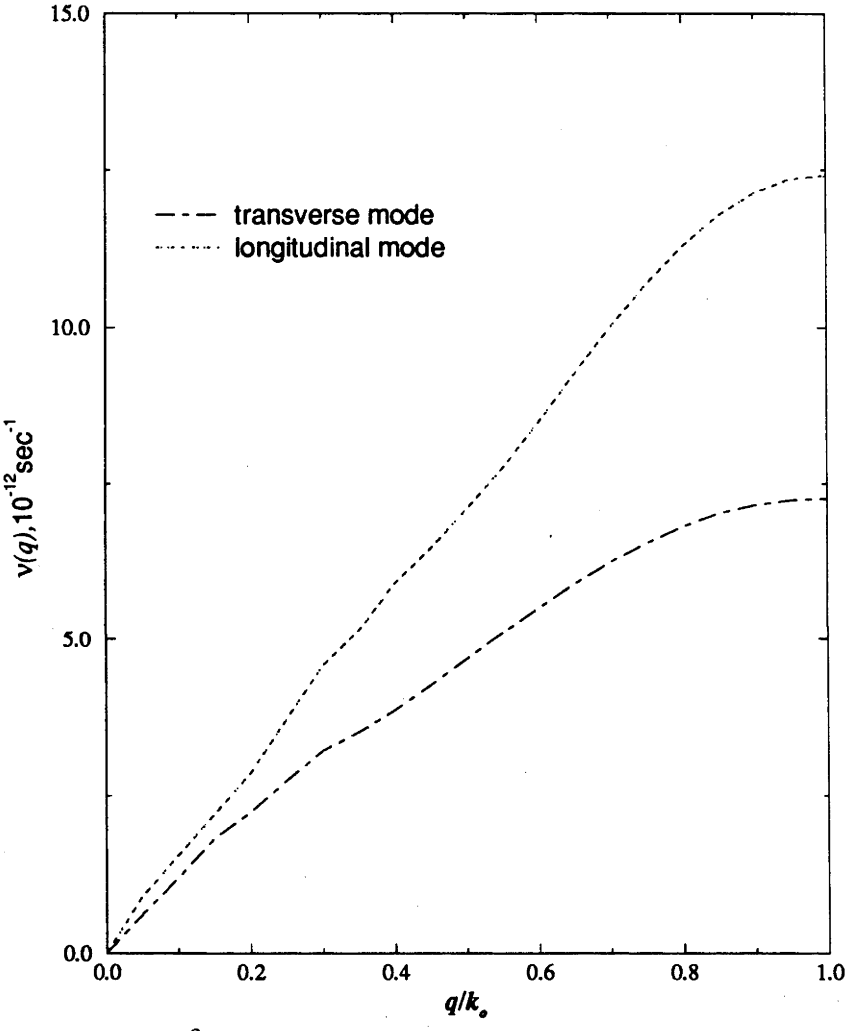

Figure 2.4: $k_o = \frac{2\pi}{a}$. The longitudinal phonon dispersion frequency of aluminium is along (1,0,0). The pseudopotential in electron-ion interaction has been taken into account here; this will be discussed in Chapter 4.

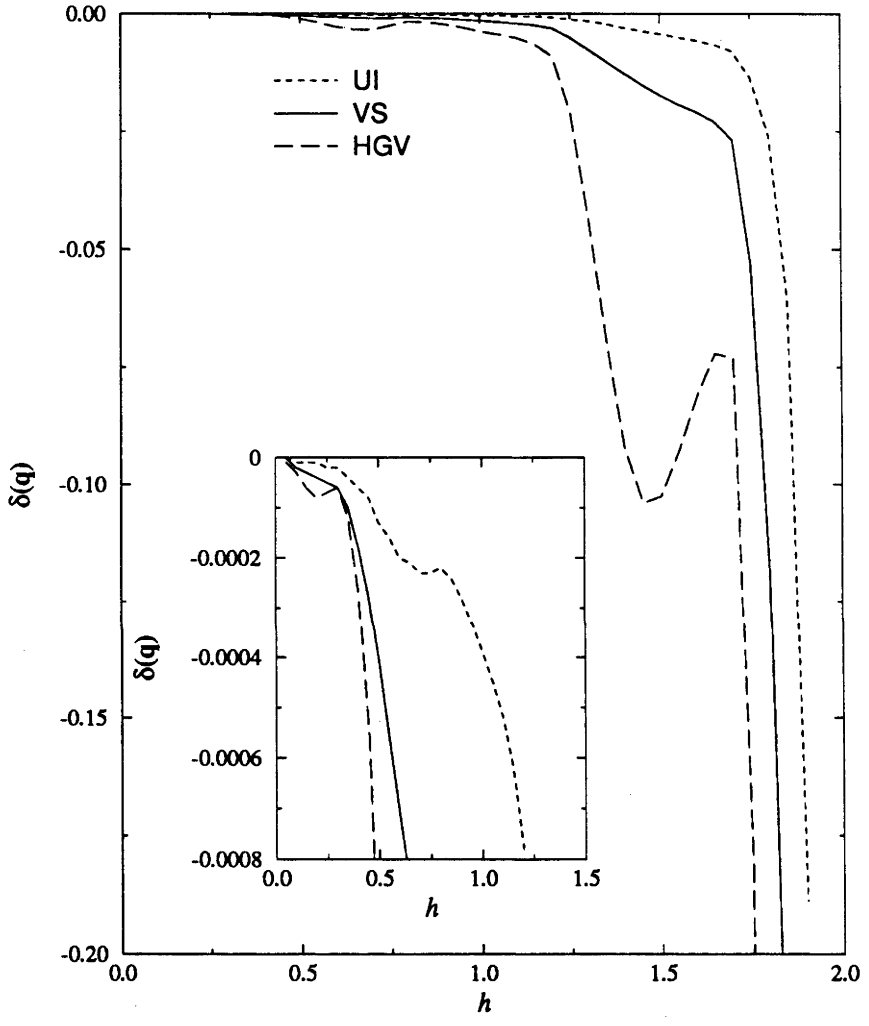

Figure 2.5: $\mathbf{h} = \mathbf{q}a/2\pi$ is along (1,0,0). $\delta(\mathbf{q}) = 1/\varepsilon_t'(\mathbf{q}) - 1/\varepsilon_t(\mathbf{q})$. $\varepsilon_t'(\mathbf{q})$ is a total dielectric function including van der Waals interaction, considered along (1,0,0)

CHAPTER 3

Dielectric Function of Alloys

A total dielectric function of alloy is discussed which has contributions from the polarisability of the electrons, and that associated with ionic displacements generally. A binary alloy NbTa is studied as an example which includes the local field correction to the electronic dielectric function. Results are shown in figure.

3.1 The equation of motion of charge fluctuations in alloys

The method followed in this section is more or less similar to that in Chapter 2. In an alloy represented by a multi-atomic lattice, the Hamiltonian for the ionic system in the presence of an external test charge density $\rho_{ext}(\mathbf{r},t)$ is given by

$$H = \sum_{\alpha}\sum_{i=1}^{N_\alpha}\frac{P_{\alpha i}^2}{2M_\alpha} + \frac{1}{2}\sum_{\alpha}\sum_{i\neq j}^{N_\alpha} V(\mathbf{R}_{\alpha i}-\mathbf{R}_{\alpha j}) + \frac{1}{2}\sum_{\alpha\neq\beta}\sum_{i,j}^{N_\alpha,N_\beta} V(\mathbf{R}_{\alpha i}-\mathbf{R}_{\beta j})$$

$$- e\sum_{\alpha}\sum_{i=1}^{N_\alpha}\int_\Omega Z_\alpha e n_e(\mathbf{r},t)V^{ie}(\mathbf{r}-\mathbf{R}_{\alpha i})d^3r + e\sum_{\alpha}\sum_{i=1}^{N_\alpha}\int_\Omega \frac{Z_\alpha \rho_{ext}(\mathbf{r},t)}{|\mathbf{R}_{\alpha i}-\mathbf{r}|}d^3r. \qquad (3.1)$$

The symbols here are same as those in Chapter 2 except the α, β, ..., which refer to the species of ions, and $(Z_\alpha e)$ is the charge of ion species α. N_α is the total number of ions of α species in the system of total volume Ω. Obviously $\sum_{i=\{\alpha,\beta,...\}} N_i$ is the total number of ions in the system. The direct interaction between the ions has two parts, one is the Coulomb potential and the other is the van der Waals interaction (which has perhaps been studied less throughly in earlier work on dielectric function). $Z_\alpha e^2 V^{ie}(\mathbf{r}-\mathbf{R}_{\alpha i})$ is the interaction potential between the ith ion of α

species at the position $\mathbf{R}_{\alpha i}$ and the valence electrons. Strong oscillations of the wave function of the electron within the limits of the ion core lead to a sharp decrease of the effective electron-ion interaction at short distances, and consequently also of the amplitude for the scattering of the electron by the ion at large momentum transfers, especially for the transition metals. The singularities of the wave function of the conduction electrons (valence electrons) within the limits of the ionic core do not play a fundamental role in the analysis of the properties of a metal. This suggests the natural idea of replacing the true interaction of an outer electron with a multi-electron ion by an effective single-particle potential which is non-local, in general [see Ziman (1965)]. The resultant pseudopotential or model potential is usually determined from first principles or by using experimental information [see Harrison (1966), Heine and Weaire (1970)]. In Chapter 2, I did not consider the pseudopotential. The reason is that the contribution of the pseudopotential would almost certainly be less than the error inherent in the theory there. I leave the discussion about it and analysis to the next chapter.

The following work is based on a simplified crystal structure, but it does not lose too much in generality. Assume that $\mathbf{u}_{\alpha i}$ is small, so that one can expand $V(\mathbf{R}_{\alpha i} - \mathbf{R}_{\alpha j})$ in a Taylor series about the equilibrium separation $\mathbf{R}_{\alpha io} - \mathbf{R}_{\alpha jo}$. Retaining up to quadratic terms in $\mathbf{u}_{\alpha i}$ and introducing the symbol $\mathbf{R}^{ij}_{\alpha\beta} \equiv \mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}$, we may write

$$\sum_{i \neq j} V(\mathbf{R}^{ij}_{\alpha\alpha}) = \sum_{i \neq j} V(\mathbf{R}^{ij}_{\alpha\alpha(o)}) + \sum_{i,j} \mathbf{u}_{\alpha i} \overleftrightarrow{\mathbf{A}}_{\alpha i \alpha j} \mathbf{u}_{\alpha j}. \tag{3.2}$$

The terms linear in $\mathbf{u}_{\alpha i}$ contribute nothing at equilibrium. Here,

$$\overleftrightarrow{\mathbf{A}}_{\alpha i \alpha j} = \frac{1}{\Omega} \sum_{\mathbf{k}} \mathbf{k}\mathbf{k} V^{\alpha\alpha}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\alpha\alpha(o)}} \qquad i \neq j, \tag{3.3a}$$

$$\overleftrightarrow{\mathbf{A}}_{\alpha i \alpha i} = -\frac{1}{\Omega} \sum_{\mathbf{k}} \sum_{j} \mathbf{k}\mathbf{k} V^{\alpha\alpha}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\alpha\alpha(o)}} \qquad i \neq j, \tag{3.3b}$$

and

$$\sum_{i,j} V(\mathbf{R}^{ij}_{\alpha\beta}) = \sum_{i,j}[V(\mathbf{R}^{ij}_{\alpha\beta(o)}) + \frac{1}{2}(\mathbf{u}_{\alpha i} - \mathbf{u}_{\beta j})\overleftrightarrow{\mathbf{A}}_{\alpha i\beta j}(\mathbf{u}_{\alpha i} - \mathbf{u}_{\beta j})]. \tag{3.4}$$

$$\overleftrightarrow{\mathbf{A}}_{\alpha i\beta j} = -\frac{1}{\Omega}\sum_{\mathbf{k}} \mathbf{k}\mathbf{k} V^{\alpha\beta}_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\alpha\beta(o)}} \qquad \alpha \neq \beta. \tag{3.5}$$

Here $V^{\alpha\alpha}_{\mathbf{k}}$ is the Fourier transform of $V(\mathbf{R}^{ij}_{\alpha\alpha})$ and $V^{\alpha\beta}_{\mathbf{k}}$ is the Fourier transform of $V(\mathbf{R}^{ij}_{\alpha\beta})$. We assume that the potential energy term among the ions is well behaved so that the Fourier transforms exist. The summation here is over all possible values of $\mathbf{k}$.

The equation of motion for the ith ion for the species α, of mass M_α, will then be

$$M_\alpha \frac{\partial^2 \mathbf{u}_{\alpha i}}{\partial t^2} = -\nabla_{\alpha i} H. \tag{3.6}$$

Substituting (3.1) into the above equations gives

$$M_\alpha \frac{\partial^2 \mathbf{u}_{\alpha i}}{\partial t^2} = -\sum_{j}^{N_\alpha} \overleftrightarrow{\mathbf{A}}_{\alpha i\alpha j}\mathbf{u}_{\alpha j} - \sum_{\beta,j}^{N_\beta} \overleftrightarrow{\mathbf{A}}_{\alpha i\beta j}(\mathbf{u}_{\alpha j} - \mathbf{u}_{\beta i})$$

$$+\nabla_{\alpha i}\sum_{\beta} Z_\beta e^2 \sum_{j}^{N_\beta}\int_\Omega n_e(\mathbf{r},t)V^{ie}(\mathbf{r}-\mathbf{R}_{\beta j})d^3r - \nabla_{\alpha i}\sum_{\beta} Z_\beta e \sum_{j}^{N_\beta}\int_\Omega \frac{\rho_{ext}(\mathbf{r},t)}{|\mathbf{r}-\mathbf{R}_{\beta j}|}d^3r. \tag{3.7}$$

3.2 $\chi_e(\mathbf{k})$ in the electron-ion system

The induced charge density from the small displacement of the ions, treating them as point charges, is

$$\rho_{ion}(\mathbf{r},t) = \sum_{\alpha} Z_\alpha e \sum_{i}^{N_\alpha}[\delta(\mathbf{r} - \mathbf{R}_{\alpha i(o)} - \mathbf{u}_{\alpha i}) - \delta(\mathbf{r} - \mathbf{R}_{\alpha i(o)})]. \tag{3.8}$$

Let the external test charge density $\rho_{ext}(\mathbf{r},t)$ be small. Then $\chi_e(\mathbf{r}-\mathbf{r}')$, a density-density response function giving the induced electron density due to an external charge density from the small displacement of the ions, may be defined through the equations (as in §2.2),

$$-en(\mathbf{r},t) = \int_{\Omega} \chi_e(\mathbf{r}-\mathbf{r}',t-t')[\rho_{ext}(\mathbf{r}',t)+\rho_{ion}(\mathbf{r}',t)]d^3r'dt'. \tag{3.9}$$

Substitution of equation (3.8) into (3.9) gives

$$\begin{aligned} en(\mathbf{r},t) &= -\Big\{\int_{\Omega} \chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t)d^3r'dt' \\ &\quad + \sum_{\alpha i} Z_\alpha e[\int \chi_e(\mathbf{r}-\mathbf{R}_{\alpha i}) - \int \chi_e(\mathbf{r}-\mathbf{R}_{\alpha i o})]dt'\Big\} \end{aligned} \tag{3.10}$$

In reciprocal space, equation (3.9) would have the form

$$-en(\mathbf{k},\omega) = (\frac{1}{\varepsilon_e(\mathbf{k},\omega)} - 1)[\rho_{ext}(\mathbf{k},\omega)+\rho_{ion}(\mathbf{k},\omega)]. \tag{3.11}$$

This follows from the procedure of Gorobchenko *et al* (1989). Here $\varepsilon_e(\mathbf{k},\omega)$ is the electronic dielectric function. Some calculation leads to (see Appendix B)

$$\chi_e(\mathbf{k}) = \frac{1}{\varepsilon_e(\mathbf{k})} - 1. \tag{3.12}$$

3.3 Dielectric function of the electron-ion system

Let us discuss the equation of motion of charge fluctuations due to ionic displacements.

The left side of equation (3.7) has the following form in Fourier space: (see Appendix A)

$$M_\alpha \frac{\partial^2 \mathbf{u}_{\alpha i}}{\partial t^2} = \frac{M_\alpha}{N_\alpha} \sum_{\mathbf{k}\in\mathbf{K}} \ddot{\mathbf{q}}_{\alpha\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}. \tag{3.13}$$

The first and second terms in the right hand side of equation (3.7) are from the interaction of the ions including the van der Waals potential. Using equations (3.3a) and (3.3b) the first term of the right hand side of the equation has the form

$$-\sum_{j}^{N_\alpha} \overleftrightarrow{\mathbf{A}}_{\alpha i \alpha j}\mathbf{u}_{\alpha j} = -\frac{1}{\Omega}\sum_{j,\mathbf{k}}^{N_\alpha} \mathbf{k}\mathbf{k}V_{\mathbf{k}}^{\alpha\alpha} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha\alpha}^{ij}}\mathbf{u}_{\alpha j} + \frac{1}{\Omega}\sum_{j,\mathbf{k}}^{N_\alpha} \mathbf{k}\mathbf{k}V_{\mathbf{k}}^{\alpha\alpha} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha\alpha}^{ij}}\mathbf{u}_{\alpha i}. \tag{3.14}$$

$\mathbf{k}$ runs over all possible values. Since the two sums are cancelled when $i = j$, the restriction $i \neq j$ has been removed. Substituting $\mathbf{u}_{\alpha j}$ for $\mathbf{q}_{\alpha \mathbf{k}}$, equation (3.14) becomes

$$-\sum_{j}^{N_\alpha} \overleftrightarrow{\mathbf{A}}_{\alpha i \alpha j} \mathbf{u}_{\alpha j} = -\frac{1}{N\Omega} \sum_{j,\mathbf{k},\mathbf{k}' \in \mathbf{K}}^{N_\alpha} \mathbf{k}\mathbf{k} V_{\mathbf{k}}^{\alpha\alpha} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha\alpha}^{ij}} \ddot{\mathbf{q}}_{\alpha \mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{R}_{\alpha j}}$$

$$+\frac{1}{N\Omega} \sum_{j,\mathbf{k},\mathbf{k}' \in \mathbf{K}}^{N_\alpha} \mathbf{k}\mathbf{k} V_{\mathbf{k}}^{\alpha\alpha} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha\alpha}^{ij}} \ddot{\mathbf{q}}_{\alpha \mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{R}_{\alpha i}}. \tag{3.15}$$

Summing over all integers j, and using (A.9), we get

$$-\sum_{j}^{N_\alpha} \overleftrightarrow{\mathbf{A}}_{\alpha i \alpha j} \mathbf{u}_{\alpha j} = -\frac{1}{\Omega} \sum_{m,\mathbf{k} \in \mathbf{K}} [(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m) V_{\mathbf{k}+\mathbf{K}_m}^{\alpha\alpha} - \mathbf{K}_m \mathbf{K}_m V_{\mathbf{K}_m}^{\alpha\alpha}] e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}} \mathbf{q}_{\alpha \mathbf{k}}. \tag{3.16}$$

Here $\mathbf{q}_{\alpha \mathbf{k}}$ is a normal coordinate. The second term of the right hand side of equation (3.7) is

$$\sum_{\beta,j}^{N_\beta} \overleftrightarrow{\mathbf{A}}_{\alpha i \beta j} (\mathbf{u}_{\beta j} - \mathbf{u}_{\alpha i}) = \frac{1}{\Omega} \sum_{m,\mathbf{k} \in \mathbf{K}} (\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m) V_{\mathbf{k}+\mathbf{K}_m}^{\alpha\beta} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}} \mathbf{q}_{\beta \mathbf{k}} e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}$$

$$-\frac{N_\beta}{N_\alpha \Omega} \sum_{m,\mathbf{k} \in \mathbf{K}} \mathbf{K}_m \mathbf{K}_m V_{\mathbf{K}_m}^{\alpha\beta} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}} \mathbf{q}_{\alpha \mathbf{k}} e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}. \tag{3.17}$$

Here the $\mathbf{R}_{\alpha\beta}$ is the smallest distance vector between α ion and β ion.

Before going on to the third term of equation (3.7), the electron density $n_e(\mathbf{r}, t)$ must be considered. That may be written as,

$$n_e(\mathbf{r}, t) = n_o + n(\mathbf{r}, t)$$

$$= n_o - \frac{1}{e} \int_\Omega \int_{-\infty}^{t} \chi_e(\mathbf{r}-\mathbf{r}', t-t')[\rho_{ext}(\mathbf{r}', t') + \rho_{ion}(\mathbf{r}', t')] d^3r' dt'$$

$$= n_o - \int_\Omega \int_{-\infty}^{t} \chi_e(\mathbf{r}-\mathbf{r}', t-t') \sum_{\alpha i} Z_\alpha [\delta(\mathbf{r}' - \mathbf{R}_{\alpha i}) - \delta(\mathbf{r}' - \mathbf{R}_{\alpha i o})] d^3r' dt'$$

$$-\frac{1}{e}\int_{\Omega}\int_{-\infty}^{t}\chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t')d^3r'dt'$$

$$=-\sum_{\alpha i}Z_\alpha\int_{-\infty}^{t}\chi_e(\mathbf{r}-\mathbf{R}_{\alpha i},t-t')dt'-\frac{1}{e}\int_{\Omega}\int_{-\infty}^{t}\chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho_{ext}(\mathbf{r}',t')d^3r'dt'. \tag{3.18}$$

Substituting this into the third term of equation (3.7) gives,

$$\nabla_{\alpha i}\sum_{\beta}Z_\beta e^2\sum_{j}^{N_\beta}\int_{\Omega}n_e(\mathbf{r},t)V^{ie}(\mathbf{r}-\mathbf{R}_{\beta j})d^3r$$

$$=-\frac{Z_\alpha e^2}{\Omega}\sum_{\beta}Z_\beta\sum_{m,\mathbf{k}\in\mathbf{K}}\int_{-\infty}^{\infty}[\chi_e(\mathbf{k}+\mathbf{K}_m,\omega)V^{ie}_{\mathbf{k}+\mathbf{K}_m}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta\mathbf{k}}(\omega)$$

$$-\frac{N_\beta}{N_\alpha}\chi_e(\mathbf{K}_m,\omega)V^{ie}_{\mathbf{K}_m}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha\mathbf{k}}(\omega)]e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}e^{-i\omega t}d\omega$$

$$-\frac{i4\pi eZ_\alpha}{\Omega}\sum_{\mathbf{k}}\frac{\mathbf{k}}{k^2}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)\rho_{ext}(\mathbf{k},\omega)e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}e^{-i\omega t}d\omega. \tag{3.19}$$

For details of the above calculation, see Appendix C. The last term of equation (3.7) is easily handled, and is given by

$$-e\nabla_{\alpha i}\sum_{\gamma j}^{N_\gamma}Z_\gamma\int_{\Omega}\frac{\rho_{ext}(\mathbf{r},t)}{|\mathbf{r}-\mathbf{R}_{\gamma j}|}d^3r=-\frac{4\pi e}{\Omega^2}\nabla_{\alpha i}\sum_{\gamma j}^{N_\gamma}Z_\gamma\int_{\Omega}\sum_{\mathbf{k}\mathbf{k}'}\frac{\rho_{ext}(\mathbf{k},t)}{k'^2}e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_{\gamma j})}d^3r$$

$$=-\frac{i4\pi Z_\alpha e}{\Omega}\sum_{\mathbf{k}}\frac{\mathbf{k}}{k^2}\rho_{ext}(\mathbf{k},t)e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}. \tag{3.20}$$

Substituting the above into equation (3.7) becomes

$$\frac{M_\alpha}{N_\alpha}\sum_{\mathbf{k}\in\mathbf{K}}\ddot{\mathbf{q}}_{\alpha\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}=$$

$$-\frac{1}{\Omega}\sum_{m,\mathbf{k}\in\mathbf{K}}[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)V^{\alpha\alpha}_{\mathbf{k}+\mathbf{K}_m}-\mathbf{K}_m\mathbf{K}_m V^{\alpha\alpha}_{\mathbf{K}_m}]e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}\mathbf{q}_{\alpha\mathbf{k}}\cdot$$

$$-\frac{1}{\Omega}\sum_{m,\mathbf{k}\in\mathbf{K}}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)V^{\alpha\beta}_{\mathbf{k}+\mathbf{K}_m}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}\mathbf{q}_{\beta\mathbf{k}}e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}$$

$$+\frac{N_\beta}{N_\alpha\Omega}\sum_{m,\mathbf{k}\in\mathbf{K}}\mathbf{K}_m\mathbf{K}_m V^{\alpha\beta}_{\mathbf{K}_m}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}\mathbf{q}_{\alpha\mathbf{k}}e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}$$

$$-\frac{Z_\alpha e^2}{2\pi\Omega}\sum_\beta Z_\beta\sum_{m,\mathbf{k}\in\mathbf{K}}\int_{-\infty}^{\infty}[\chi_e(\mathbf{k}+\mathbf{K}_m,\omega)V^{ie}_{\mathbf{k}+\mathbf{K}_m}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta\mathbf{k}}(\omega)$$

$$-\frac{N_\beta}{N_\alpha}\chi_e(\mathbf{K}_m,\omega)V^{ie}_{\mathbf{K}_m}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha\mathbf{k}}(\omega)e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}e^{-i\omega t}d\omega$$

$$-\frac{i4\pi eZ_\alpha}{2\pi\Omega}\sum_{\mathbf{k}}\frac{\mathbf{k}}{k^2}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)\rho_{ext}(\mathbf{k},\omega)e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}e^{-i\omega t}d\omega$$

$$-\frac{i4\pi Z_\alpha e}{\Omega}\sum_{\mathbf{k}}\frac{\mathbf{k}}{k^2}\rho_{ext}(\mathbf{k},t)e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}. \tag{3.21}$$

Taking a solution of the form

$$\mathbf{q}_{\alpha\mathbf{k}}(t)\propto e^{i\omega t}$$

and using the relation

$$\chi_e(\mathbf{k},\omega)=\frac{1}{\varepsilon_e(\mathbf{k},\omega)}-1 \tag{3.22}$$

equation (3.21) can be simplified to the form

$$-\frac{M_\alpha}{N_\alpha}\omega^2\mathbf{q}_{\alpha k}(\omega)=-\frac{1}{\Omega}\sum_{\beta m}\Big[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta k}W^{\alpha\beta}(\mathbf{k}+\mathbf{K}_m)$$

$$-\frac{N_\beta}{N_\alpha}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha k}W^{\alpha\beta}(\mathbf{K}_m)\Big]\,e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}-\frac{i4\pi eZ_\alpha\mathbf{k}\rho_{ext}(\mathbf{k},\omega)}{\Omega k^2\varepsilon_e(\mathbf{k},\omega)}. \tag{3.23}$$

Here pure Couloumb interaction is taken between electrons and ions. Later, the pseudopotential will be brought into the equation. The $W^{\alpha\beta}(\mathbf{k})$ is defined as,

$$W^{\alpha\beta}(\mathbf{k})=V^{\alpha\beta}(\mathbf{k})+(\frac{1}{\varepsilon_e(\mathbf{k},\omega)}-1)V^{ie}_{\mathbf{k}}Z_\alpha Z_\beta e^2. \tag{3.24}$$

Again we consider the contribution to the induced charge only from the induced polarisation associated with ionic displacements from equilibrium positions. The total induced charge density $\rho_{in}(\mathbf{r},t)$ should be

$$\rho_{in}(\mathbf{r},t)=-en(\mathbf{r},t)+\rho_{ion}(\mathbf{r},t). \tag{3.25}$$

Its form in reciprocal space is

$$\rho_{in}(\mathbf{k},\omega)=-en(\mathbf{k},\omega)+\rho_{ion}(\mathbf{k},\omega). \tag{3.26}$$

The external test charge is assumed to have the form in space and time,

$$\rho_{ext}(\mathbf{r},t)=\frac{1}{\Omega}\rho_{ext}(\mathbf{k}_o,\omega_o)e^{i\mathbf{k}_o\cdot\mathbf{r}-i\omega_o t}. \tag{3.27}$$

From equations (3.8), (3.11), (3.26) and (3.27), a brief calculation leads to

$$\rho_{in}(\mathbf{k_o},\omega_o)=(\frac{1}{\varepsilon_e(\mathbf{k}_o,\omega_o)}-1)\rho_{ext}(\mathbf{k}_o,\omega_o)-\sum_\alpha\frac{iZ_\alpha e\mathbf{k}_o\cdot\mathbf{q}_{\alpha k_o}}{\varepsilon_e(\mathbf{k}_o,\omega_o)}. \tag{3.28}$$

3.4 Dielectric function in multi-component plasma system

In the long wavelength limit the system of free electrons and ions can be regarded as a multi-component plasma. For getting a dielectric function for multi-plasma system, equation (3.23) must be solved to determine the total dielectric function

in the general case. In the long wavelength limit, in other words for $\mathbf{k} \longrightarrow 0$, the equation (3.23) has a form:

$$-\frac{M_\alpha}{N_\alpha}\omega^2 \mathbf{q}_{\alpha k}(\omega) = -\frac{1}{\Omega}\sum_{\beta m} \mathbf{k}\mathbf{k}\cdot\mathbf{q}_{\beta k} W^{\alpha\beta}(\mathbf{k}) - \frac{i4\pi e Z_\alpha \mathbf{k}\rho_{ext}(\mathbf{k},\omega)}{\Omega k^2 \varepsilon_e(\mathbf{k},\omega)}. \tag{3.29}$$

For small k, the longitudinal ion plasma frequency for each ion species α (ignoring the interaction with electrons) is assumed of the form $\omega^2_{I(\alpha)}(\mathbf{k}) = \omega^2_{I(\alpha)} + \beta^2_{I(\alpha)}k^2$, it is easily shown that

$$\frac{k^2 W^{\alpha\beta}_{\mathbf{k}}}{4\pi Z_\alpha Z_\beta e^2} = \begin{cases} \frac{1}{\varepsilon_e(\mathbf{k},\omega)} + \frac{\beta^2_\alpha k^2}{\omega^2_\alpha} & \text{if } \alpha = \beta \\ \frac{1}{\varepsilon_e(\mathbf{k},\omega)} & \text{otherwise} \end{cases} \tag{3.30}$$

where $\omega^2_\alpha = \frac{4\pi(Z_\alpha e)^2 N_\alpha}{M_\alpha \Omega}$.

In the small $\mathbf{k}$ region, by solving the equation (3.29) (for details of algebraic work, see Appendix D), we can get,

$$Z_\alpha e\mathbf{k}\cdot\mathbf{q}_{\alpha\mathbf{k}} = -\frac{i\rho_{ext}(\mathbf{k}_o,\omega_o)}{\Omega_\alpha(1+\sum_\beta \frac{1}{\Omega_\beta})}. \tag{3.31}$$

Here $\Omega_\alpha = \frac{\beta^2_\alpha k^2 - \omega^2}{\omega^2_\alpha}\varepsilon_e(\mathbf{k},\omega)$.

The definition of the inverse of the total longitudinal dielectric function $\varepsilon_t(\mathbf{k},\omega)$ is

$$\frac{1}{\varepsilon_t(\mathbf{k},\omega)} = 1 + \frac{\rho_{in}(\mathbf{k},\omega)}{\rho_{ext}(\mathbf{k},\omega)}. \tag{3.32}$$

The form of the electronic dielectric function at long wavelengths is,

$$\frac{1}{\varepsilon_e(\mathbf{k},\omega)} = 1 - \frac{\omega_p^2}{\omega_p^2 + \beta_e^2 k^2 - \omega^2}. \tag{3.33}$$

We finally get the total dielectric function through equation (3.28),

$$\varepsilon_t(\mathbf{k},\omega) = 1 - \frac{\omega_e^2}{\omega^2 - \beta_e^2 k^2} - \sum_\alpha \frac{\omega_\alpha^2}{\omega^2 - \beta_\alpha^2 k^2}. \tag{3.34}$$

We take equation (3.34) as a simple example to discuss briefly how and where $\varepsilon_t(\mathbf{k},0)$ can be negative. Since β_e^2 is positive, the only possibility for the total static dielectric function to be negative for small $\mathbf{k}$ is that at least some of the β_α^2 are negative. The comments given in the beginning of §2.4 are applicable in this case also. In the next section, a more general total dielectric function of a binary alloy is evaluated.

3.5 Dielectric function of a binary alloy

Here a transition-metal binary alloy such as NbTa is considered – they are isoelectronic ions. Each cell contains one ion of each type with alternate positions corresponding to body-centre-cubic structure. That means $N_\alpha = N_\beta$ and $Z_\alpha = N_\beta$ in 3.1. The equation of motion of each normal coordinate, using equation (3.23), are respectively,

$$-\frac{\omega^2}{\omega_\alpha^2}\mathbf{q}_{\alpha k} = -\frac{N_\alpha}{\Omega M_\alpha \omega_\alpha^2}\sum_m \Big\{\Big[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\alpha}_{\mathbf{k}+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m W^{\alpha\alpha}_{\mathbf{K}_m}\Big]\mathbf{q}_{\alpha k}$$

$$+\Big[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\beta}_{\mathbf{k}+\mathbf{K}_m}\mathbf{q}_{\beta k} - \mathbf{K}_m\mathbf{K}_m W^{\alpha\beta}_{\mathbf{K}_m}\mathbf{q}_{\alpha k}\Big]e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}\Big\}$$

$$-\frac{i\mathbf{k}\rho_{ext}(\mathbf{k},\omega)}{Z_\alpha e k^2 \varepsilon_e(\mathbf{k},\omega)}, \tag{3.35a}$$

$$-\frac{\omega^2}{\omega_\beta^2}\mathbf{q}_{\beta k} = -\frac{N_\beta}{\Omega M_\beta \omega_\beta^2}\sum_m \Big\{\Big[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\beta\beta}_{\mathbf{k}+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m W^{\beta\beta}_{\mathbf{K}_m}\Big]\mathbf{q}_{\beta k}$$

$$+\Big[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\beta}_{\mathbf{k}+\mathbf{K}_m}\mathbf{q}_{\alpha k} - \mathbf{K}_m\mathbf{K}_m W^{\alpha\beta}_{\mathbf{K}_m}\mathbf{q}_{\beta k}\Big]e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}\Big\}$$

$$-\frac{i\mathbf{k}\rho_{ext}(\mathbf{k},\omega)}{Z_\alpha e k^2 \varepsilon_e(\mathbf{k},\omega)}. \tag{3.35b}$$

Adding (3.35a) and (3.35b), gives,

$$-\frac{\omega^2}{\omega_\alpha^2}\mathbf{q}_{\alpha k} - \frac{\omega^2}{\omega_\beta^2}\mathbf{q}_{\beta k} = -\frac{N_\alpha}{\Omega M_\alpha \omega_\alpha^2}\sum_m \Big\{\Big[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\alpha}_{\mathbf{k}+\mathbf{K}_m} - \mathbf{K}_m\mathbf{K}_m W^{\alpha\alpha}_{\mathbf{K}_m}\Big]$$

$$+\left[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\beta}_{\mathbf{k}+\mathbf{K}_m}-\mathbf{K}_m\mathbf{K}_m W^{\alpha\beta}_{\mathbf{K}_m}\right]e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}\Big\}(\mathbf{q}_{\alpha k}+\mathbf{q}_{\beta k})$$

$$-\frac{2i\mathbf{k}\rho_{ext}(\mathbf{k},\omega)}{Z_\alpha e k^2\varepsilon_e(\mathbf{k},\omega)} \tag{3.36}$$

where the approximation is made that $W^{\alpha\alpha}_{\mathbf{k}}=W^{\beta\beta}_{\mathbf{k}}$. The reason to obtain sum of (3.35a) and (3.35b) is due to mathematical cause (see equation (3.12)). Considering (3.24), this is a reasonable approximation since the difference between them is about the difference of their pseudopotential and van der Waals interaction. At the static limit, $\omega=0$, the equation (3.36) has a simple form,

$$\mathbf{q}_{\alpha k}+\mathbf{q}_{\beta k}=-\Phi^{-1}(\mathbf{k})\frac{2i\mathbf{k}}{Z_\alpha e k^2\varepsilon(\mathbf{k})}\rho_{ext}(\mathbf{k}) \tag{3.37}$$

with

$$\Phi(\mathbf{k})=\frac{N_\alpha}{\Omega M_\alpha\omega_\alpha^2}\sum_m\Big\{\left[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\alpha}_{\mathbf{k}+\mathbf{K}_m}-\mathbf{K}_m\mathbf{K}_m W^{\alpha\alpha}_{\mathbf{K}_m}\right]$$

$$+\left[(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)W^{\alpha\beta}_{\mathbf{k}+\mathbf{K}_m}-\mathbf{K}_m\mathbf{K}_m W^{\alpha\beta}_{\mathbf{K}_m}\right]e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}\Big\}. \tag{3.38}$$

This is the dynamic vibration matrix of the binary alloy. The total induced charge density, then, is

$$\rho_{in}(\mathbf{k})=\left(\frac{1}{\varepsilon(\mathbf{k})}-1\right)\rho_{ext}(\mathbf{k})-\frac{2\mathbf{k}\cdot\Phi^{-1}\cdot\mathbf{k}}{k^2\varepsilon_e^2(\mathbf{k})}\rho_{ext}(\mathbf{k}). \tag{3.39}$$

which leads the solution of the total static dielectric function in the binary system,

$$\frac{1}{\varepsilon_t(\mathbf{k})}=\frac{1}{\varepsilon_e(\mathbf{k})}-\frac{2\mathbf{k}\cdot\Phi^{-1}\cdot\mathbf{k}}{k^2\varepsilon_e^2(\mathbf{k})}, \tag{3.40}$$

This is the total dielectric function sought. Theoretical discussion of total dielectric function for a binary alloy with an ideal structure is analytically completed at this stage. There is a technical difficulty for further discussion numerically along

with the formula (3.38). Therefore I attempt in the following to develop formula for matrix $\Phi(\mathbf{k})$ along lines similar to what I have done in Chapter 2. With the formula (3.38), there is the same difficulty that occurred as in Chapter 2 in the numerical calculation for the summation in the dynamic vibration matrix $\Phi(\mathbf{k})$, caused by the Coulomb potential between ions, because of the slow convergence of the sums. From the idea of Ewald's sums, the dynamic vibration matrix $\Phi(\mathbf{k})$ can be written as follow. The details of the process can be obtained from Appendix E.

$$\begin{aligned}\Phi(\mathbf{k}) &= \sum_m [(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)F_c(\mathbf{k}+\mathbf{K}_m) - \mathbf{K}_m\mathbf{K}_m F_c(\mathbf{K}_m)]\,(1+e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}) \\ &\quad -\frac{\Omega}{4\pi N_\alpha}\sum_j \left[\mathbf{T}^{ij}_{\alpha\alpha}+\mathbf{T}^{ij}_{\alpha\beta}\right] \\ &\quad +\frac{\Omega}{4\pi(Z_\alpha e)^2 N_\alpha}\sum_j \left[\mathbf{Y}^{ij}_{\alpha\alpha}+\mathbf{Y}^{ij}_{\alpha\beta}\right] \\ &\quad +\sum_m [(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\Psi(\mathbf{k}+\mathbf{K}_m) - \mathbf{K}_m\mathbf{K}_m\Psi(\mathbf{K}_m)]\,(1+e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}),\end{aligned} \tag{3.41}$$

where

$$F_c(\mathbf{k}) = \frac{\exp(-\mathbf{k}^2/4\eta)}{\mathbf{k}^2}, \tag{3.42}$$

$$\mathbf{Y}^{ij}_{\alpha\beta} = (e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\alpha\beta}}-1)\nabla_{\alpha i}\nabla_{\beta i}V_{vd}(\mathbf{R}^{ij}_{\alpha\beta}), \tag{3.43}$$

$$V_{vd}(r) = -\frac{3\hbar}{r^6\pi}\int_0^\infty \frac{d\xi\cdot\xi^4\alpha_\alpha(i\xi)\alpha_\beta(i\xi)}{(\omega_e^2+\xi^2)^2}, \tag{3.44}$$

$$\alpha_i(i\xi) = \frac{e^2 n_i}{m(\omega_i^2+\xi^2)}, \tag{3.45}$$

$$\begin{aligned}\mathbf{T}^{ij}_{\alpha\beta} &= (e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\beta\alpha}}-1) \\ &\times \left[G^{ij}_{\beta\alpha}\left(\frac{3}{(R^{ij}_{\beta\alpha})^2}\mathbf{R}^{ij}_{\beta\alpha}\mathbf{R}^{ij}_{\beta\alpha}-\mathbf{I}\right)+H^{ij}_{\beta\alpha}\left(2\left(\frac{3}{2(R^{ij}_{\beta\alpha})^2}+\eta\right)\mathbf{R}^{ij}_{\beta\alpha}\mathbf{R}^{ij}_{\beta\alpha}-\mathbf{I}\right)\right],\end{aligned}$$

(3.46)

$$\Psi(\mathbf{k}) = (\frac{1}{\varepsilon_e(\mathbf{k})} - 1)V^{ie}(\mathbf{k}). \tag{3.47}$$

$\alpha_\beta(i\xi)$ is electric dipole polarisability of the ion species β.

For equations (3.44) which is van der Waals interaction, and (3.45) which gives a formula for the electric dipole polarisability of ion species β, see Mahanty and Taylor (1978).

The coefficient of the $(1/r^6)$ term in (3.44) is

$$\begin{aligned} \tau_{\alpha\beta} &= -\frac{3\hbar}{\pi}\int_0^\infty \frac{d\xi \cdot \xi^4 \alpha_\alpha(i\xi)\alpha_\beta(i\xi)}{(\omega_e^2+\xi^2)^2} \\ &= -\frac{3\hbar\alpha_\alpha(0)\alpha_\beta(0)[2\omega_\alpha\omega_\beta - 3\omega_p(\omega_\alpha+\omega_\beta)]}{2(\omega_\alpha+\omega_\beta)}. \end{aligned} \tag{3.48}$$

The excitation energy in formula (3.44) has the form:

$$\omega_i = \sqrt{\frac{e^2 n_i}{m\alpha_i(0)}} = \frac{e^2}{\hbar}\sqrt{\frac{a_o n_i}{\alpha_i(0)}}. \tag{3.49}$$

Here is a list of relevant data for Ta and Nb calculated through (3.45), which will be used in later numerical work:

$$Ta^{+5}: \begin{cases} n_{Ta} = 68 \\ \alpha_{Ta}(0) = 0.45(\mathring{A}^3) \\ \omega_{Ta} = \frac{e^2}{\hbar}\sqrt{\frac{n_{Ta}a_o}{\alpha_{Ta}(0)}} = 19.57 \times 10^{16} s^{-1} \end{cases}$$

$$Nb^{+5}: \begin{cases} n_{Nb} = 36 \\ \alpha_{Nb}(0) = 0.35(\mathring{A}^3) \\ \omega_{Nb} = \frac{e^2}{\hbar}\sqrt{\frac{n_{Nb}a_o}{\alpha_{Nb}(0)}} = 16.24 \times 10^{16} s^{-1} \end{cases}$$

Equation (3.41), when van der Waals interaction in included, can be written as

$$\Phi_{ii}(\mathbf{h}) = S_{ii} + \sum_m [F(\mathbf{h}+\mathbf{m})(h_i+m_i)(h_i+m_i) - F(\mathbf{m})m_i m_i](1+\cos(m\pi))$$

$$-\frac{\Omega}{4\pi N_\alpha}\sum_l \left\{(c_l-1)\left[G_l(\frac{3l_i^2}{l^2}-1) + H_l[2(\frac{3}{2l^2}+a^2\eta)l_i^2 - 1]\right]\right.$$

$$\left.+(c_{l'}-1)\left[G_{l'}(\frac{3(l_i+\frac{1}{2})^2}{l'^2}-1) + H_{l'}[2(\frac{3}{2l'^2}+a^2\eta)(l_i+\frac{1}{2})^2 - 1]\right]\right\}$$

$$+\frac{\Omega}{4\pi(Z_\alpha e)^2 N_\alpha}\sum_l \left[(c_l-1)(\frac{-6}{l^8}+\frac{48l_i^2}{l^{10}})\frac{\tau_{\alpha\alpha}}{a^8} + (c_{l'}-1)(\frac{-6}{l'^8}+\frac{48(l_i+\frac{1}{2})^2}{l'^{10}})\frac{\tau_{\alpha\beta}}{a^8}\right], \tag{3.50a}$$

$$\Phi_{ij}(\mathbf{h}) = S_{ij} + \sum_m [F(\mathbf{h}+\mathbf{m})(h_i+m_i)(h_j+m_j) - F(\mathbf{m})m_i m_j](1+\cos(m\pi))$$

$$-\frac{\Omega}{4\pi N_\alpha}\sum_l \left\{(c_l-1)\left[G_l\frac{3l_i l_j}{l^2} + 2H_l(\frac{3}{2l^2}+a^2\eta)l_i l_j\right]\right.$$

$$\left.+(c_{l'}-1)\left[G_{l'}\frac{3(l_i+\frac{1}{2})(l_j+\frac{1}{2})}{l'^2} + 2H_{l'}(\frac{3}{2l'^2}+a^2\eta)(l_i+\frac{1}{2})(l_j+\frac{1}{2})\right]\right\}$$

$$+\frac{\Omega}{4\pi(Z_\alpha e)^2 N_\alpha}\sum_l \left[(c_l-1)\frac{48l_i l_j}{l^{10}}\frac{\tau_{\alpha\alpha}}{a^8} + (c_{l'}-1)\frac{48(l_i+\frac{1}{2})(l_i+\frac{1}{2})}{l'^{10}})\frac{\tau_{\alpha\beta}}{a^8}\right] \tag{3.50b}$$

where

$$\mathbf{h} = \frac{2\pi}{a}\mathbf{k},$$

$$l = \sqrt{l_1^2 + l_2^2 + l_3^2},$$

$$l' = \sqrt{(l_1+\frac{1}{2})^2 + (l_2+\frac{1}{2})^2 + (l_3+\frac{1}{2})^2},$$

$$c_l = \cos(2\pi(h_1 l_1 + h_2 l_2 + h_3 l_3)),$$

$$c_{l'} = \cos[2\pi(h_1(l_1 + \frac{1}{2}) + h_2(l_2 + \frac{1}{2}) + h_3(l_3 + \frac{1}{2}))],$$

$$s_{ij} = 2F(h)h_i h_j,$$

$$F(x) = \exp(-\pi^2 x^2/(a^2\eta))/x^2 + (\frac{1}{\varepsilon_e(h)} - 1)V^{ie}(h),$$

$$G_l = \frac{1 - G(a\eta^{\frac{1}{2}}l)}{a^3 l^3},$$

$$G(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-s^2)ds,$$

$$H_l = 2(\frac{\eta}{\pi})^{\frac{1}{2}} \frac{\exp(-\eta a^2 l^2)}{a^2 l^2}.$$

3.6 Calculation of the dielectric function and results

In this section, some calculation of the dielectric function will be carried out. From the equation (3.40), the dielectric function can be written as the following by using the assumptions in the last section,

$$\frac{1}{\varepsilon_t(\mathbf{h})} = \frac{1}{\varepsilon_e(\mathbf{h})} - \frac{2\mathbf{h} \cdot \Phi^{-1}(\mathbf{h}) \cdot \mathbf{h}}{\varepsilon_e^2(\mathbf{h})|\mathbf{h}|^2}, \tag{3.52}$$

where the usual expression for the electronic dielectric function is used with the static local-field correction $G(\mathbf{k})$,

$$\varepsilon_e(\mathbf{k}) = 1 - \frac{V(\mathbf{k})\chi_o(\mathbf{k})}{1 + V(\mathbf{k})\chi_o(\mathbf{k})G(\mathbf{k})} \tag{3.53}$$

$\chi_o(\mathbf{k})$ is given by Lindhard's formula,

$$\chi_o(\mathbf{k}) = -\frac{mk_F}{\pi^2\hbar^2}\left[\frac{1}{2} + \frac{1-x^2}{4x}\ln\left|\frac{1+x}{1-x}\right|\right] \tag{3.54}$$

where k_F is Fermi wave vector and $x = k/2k_F$.

In the following numerical calculation, $G(\mathbf{k})$ the local field correction, is taken from the data of Utsumi-Ichimaru approximation [see Dolgov and Maksimov (1989)].

Figure 3.1 is the static electronic dielectric function which is obtained by slightly changing the dielectric function based on Utsumi-Ichimaru local-field correction, this change being necessary to ensure physical stability of the system. The change is done by adding a small number to the term $(1 + V(\mathbf{q})\chi_o(\mathbf{q})G(\mathbf{q}))$ in the denominater in the expression for $\varepsilon_e(\mathbf{q})$. This approach became necessary because with the available data that I have used, the alloy NbTa developed structural instability (i.e., the longitudinal dispersion curve became negative at some values of $\mathbf{q}$).

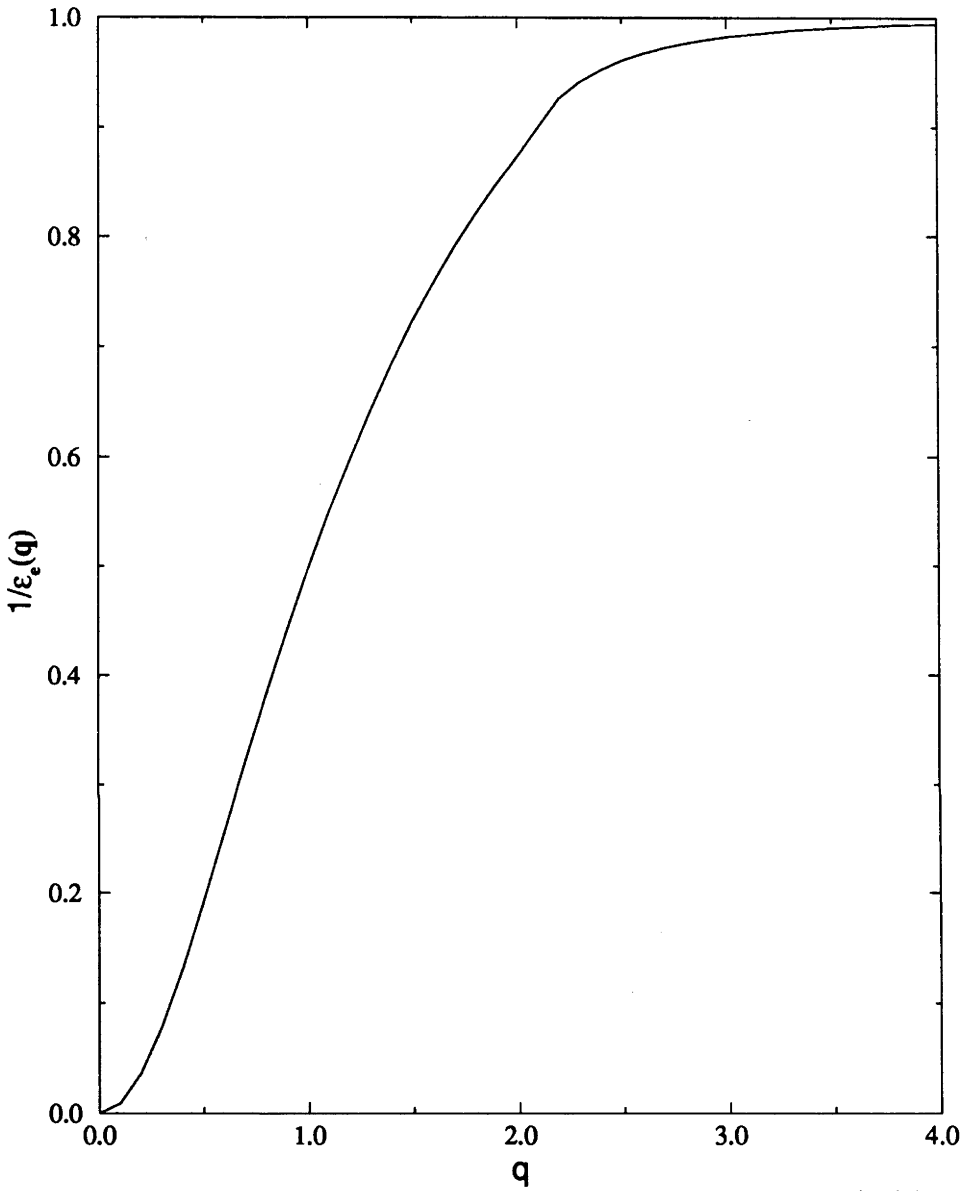

Figure 3.1: This is a static electronic dielectric function $1/\varepsilon_e(q)$ for NbTa which is modified by slightly changing the expression based on Utsumi-Ichimaru local-field correction, as explained in p.55.

CHAPTER 4

The Effect of Pseudopotentials on the Dielectric Function

The concept of a pseudopotential was first introduced by Phillips and Kleinman (see Phillips (1959) and Phillips and Kleinman (1959), Harrison (1966) and Yastrebov and Katsnelson (1987)) while developing simplified techniques for computing the energy bands in semiconductors. The inner core electrons in atoms have very little role in the solid state properties, therefore it is useful to replace the true potential by the pseudopotential. The literature on the pseudopotentials is very vast and unfortunately there is no unique way to construct a pseudopotential. The general philosophy has been to replace a strong real potential by a weak model pseudopotential so that perturbative calculations can be effectively implemented.

In this chapter simple model pseudopotentials have been used in constructing the total dielectric function and the results are compared with those obtained from the bare Coulomb potential.

4.1 Models of pseudopotentials

The Hamiltonian for the electrons which are interacting with each other and with ions is written in the second quantised form,

$$\hat{H} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} a^+_{\mathbf{k}} a_{\mathbf{k}} + \frac{1}{2} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} \frac{4\pi e^2}{\Omega q^2} a^+_{\mathbf{k}-\mathbf{q}} a^+_{\mathbf{k}'+\mathbf{q}} a_{\mathbf{k}'} a_{\mathbf{k}} + \sum_{\mathbf{kq}} U_{\mathbf{k},\mathbf{k}+\mathbf{q}} a^+_{\mathbf{k}} a_{\mathbf{k}+\mathbf{q}}, \qquad (4.1)$$

where the interaction of the electron with the ion system is

$$U_{\mathbf{k},\mathbf{k+q}} = V^{ie}(\mathbf{k},\mathbf{k}+\mathbf{q})\frac{1}{N}\sum_{m}\exp(i\mathbf{q}\cdot\mathbf{R_m}). \tag{4.2}$$

N is the total number of ions. A plane wave representation for the electrons is used here. $V^{ie}(\mathbf{k},\mathbf{k}+\mathbf{q})$ is electron-ion interaction.

In terms of U the general form of the ground-state energy of the electron system can be expressed in a series as

$$E_e = E^{(0)} + E^{(1)} + E^{(2)} + E^{(3)} + \ldots, \tag{4.3}$$

where

$$E^{(n)} = \Omega \sum_{\mathbf{q_1}\ldots\mathbf{q_n}} \Gamma^{(n)}(\mathbf{q_1}\ldots\mathbf{q_n})U_{\mathbf{q_1}}\ldots U_{\mathbf{q_n}}\Delta(\mathbf{q_1}+\ldots+\mathbf{q_n}). \tag{4.4}$$

The quantity $\Gamma^{(n)}$ is a many-pole function [see Brovman and Kagan 1974 for details]. It depends only on the electron-electron interaction and does not depend on the position of the ions or on the properties of the particular ion. $\Delta(\mathbf{q})$ takes care of the momentum conservation law corresponding to homogeneity of space.

In the general case, $V^{ie}_{\mathbf{k},\mathbf{k+q}}$ is non-local. When it is reduced to a local form, the matrix element depends only on the momentum difference $\mathbf{q}$,

$$V^{ie}_{\mathbf{k},\mathbf{k+q}} \longrightarrow V^{ie}_{\mathbf{q}}.$$

With all these, the electronic contribution to the dynamical matrix [see Brovman and Kagan 1974] for an elemental metal is

$$\begin{aligned}\Phi^{(n)} \;=\; & \Omega\frac{n(n-1)}{M}\sum_{\mathbf{K_1},\ldots,\mathbf{K_n}}[\,(\mathbf{q}+\mathbf{K_1})(\mathbf{q}+\mathbf{K_2}) \\ & \times\Gamma^{(n)}(\mathbf{q}+\mathbf{K_1},-\mathbf{q}-\mathbf{K_2},\mathbf{K_3},\ldots,\mathbf{K_n})V^{ie}_{\mathbf{q}+\mathbf{K_1}}V^{ie}_{-\mathbf{q}-\mathbf{K_2}}V^{ie}_{\mathbf{K_3}}\ldots V^{ie}_{\mathbf{K_n}} \\ & \times\Delta(\mathbf{K_1}-\mathbf{K_2}+\mathbf{K_3}+\ldots+\mathbf{K_n}).\end{aligned} \tag{4.5}$$

In the second order approximation ($n = 2$), $\Gamma^{(2)}$ has the form (see Brovman and Kagan 1974)

$$\Gamma^{(2)}(\mathbf{q},-\mathbf{q}) = -\frac{1}{2}\frac{\pi(\mathbf{q})}{\varepsilon_e(\mathbf{q})}, \tag{4.6}$$

where

$$\pi(\mathbf{q}) = (\varepsilon_e(\mathbf{q}) - 1)\frac{q^2\Omega_o}{4\pi e^2}. \tag{4.7}$$

Ω_o is the volume per ion and $\varepsilon_e(\mathbf{q})$ is the static dielectric function of the homogeneous electron gas. In accordance with equation (4.5) the second order of dynamical matrix of an elemental metal takes the form

$$\Phi^{(2)}(\mathbf{q}) = -\sum_m \left[\frac{(\mathbf{q}+\mathbf{K}_m)(\mathbf{q}+\mathbf{K}_m)}{|\mathbf{q}+\mathbf{K}_m|^2}\Psi(\mathbf{q}+\mathbf{K}_m) - \frac{\mathbf{K}_m\mathbf{K}_m}{|\mathbf{K}_m|^2}\Psi(\mathbf{K}_m)\right], \tag{4.8}$$

where $\Psi(\mathbf{q})$ is given by

$$\Psi(\mathbf{q}) = \frac{|V^{ie}(\mathbf{q})|^2\pi(\mathbf{q})q^2}{\varepsilon_e(\mathbf{q})}\frac{\Omega_o}{4\pi z^2e^2}, \tag{4.9}$$

$V^{ie}(\mathbf{q}) = V^{ie}_{\mathbf{q}}$. The function $\Psi(\mathbf{q})$ includes information about both the pseudopotential and the electron dielectric function $\varepsilon_e(\mathbf{q})$. Here the data for $\Psi(\mathbf{q})$ used in numerical calculations is taken from Animalu's paper (1966) for aluminium.

The longitudinal phonon dispersion of metals can be easily worked out as

$$\begin{aligned}\omega_L^2(\mathbf{q}) &= \frac{\mathbf{q}\cdot\Phi(\mathbf{q})\cdot\mathbf{q}}{|\mathbf{q}|^2} \\ &= \sum_{m=0}\omega_{pl}^2\left[\frac{(\mathbf{q}\cdot(\mathbf{q}+\mathbf{K}_m))^2}{q^2|\mathbf{q}+\mathbf{K}_m|^2}(1-\Psi(\mathbf{q}+\mathbf{K}_m)) - \frac{(\mathbf{q}\cdot\mathbf{K}_m)^2}{q^2|\mathbf{K}_m|^2}(1-\Psi(\mathbf{K}_m))\right]\end{aligned} \tag{4.10}$$

where $\omega_{pl}^2 = 4\pi Z^2e^2N/M$, the ion plasma frequency.

Within this theory, the total dielectric function can be obtained [see Dolgov and Maksimov (1978) and Dolgov *et al* (1981)] as

$$\frac{1}{\varepsilon_t(\mathbf{q},0)} = \frac{1}{\varepsilon_e(\mathbf{q},0)}\left[1 - \frac{\omega_{pl}^2}{\varepsilon_e(\mathbf{q},0)\omega_L^2(\mathbf{q})}\left(\frac{V^{ie}(\mathbf{q})}{V_c(\mathbf{q})}\right)^2\right], \tag{4.11}$$

where $V_c(\mathbf{q})$ represents the pure Coulombic potential between electrons and ions.

In figure 4.1, the inverse of the total dielectric function for aluminium has been shown as a function of $\mathbf{q}$. When the pseudopotential is included, the dielectric function becomes more negative in most regions of $\mathbf{q}$ space. Solid line represents the total dielectric function by taking pseudopotential into consideration. Dashed line represents the total dielectric function with pure Coulomb potential.

Figure 4.2 shows a comparison of the total dielectric function $\varepsilon_t(\mathbf{k})$ under three different choices of local-field correction by including the same pseudopotential as in figure 4.1. These choices are due to UI, VS and HGV, discussed earlier in §2.5

These results will be used in the calculation of the BCS gap equation in the next section.

In the next example the correction to the dielectric function of the binary alloy NbTa due to inclusion of pseudopotentials discussed. The pseudopotential descriptions for simple metals is quite satisfactory generally. However, the situation for the transition metals is not so favourable. Here a simple form of a model pseudopotential of a bare ion [see Heine (1970)] is used,

$$V^{ie}(r) = \begin{cases} -Ze^2/r & \text{if } r > R \\ A & \text{otherwise} \end{cases} \tag{4.12}$$

In reciprocal space, this has the form (Yastrebov *et al* (1987))

$$V^{ie}(\mathbf{q}) = -\frac{4\pi}{\Omega_o}\frac{q(Ze^2 - AR)\cos(qR) + A\sin(qR)}{q^3} \tag{4.13}$$

where the value of A is taken as either 0 or $-Ze^2/R$. It has been suggested [see Heine (1970)] that $R > R_c$, the atomic radius. In several calculation, R is chosen to be equal to R_c. If $A = 0$ (Ashcroft model)

$$V^{ie}(\mathbf{q}) = -\frac{4\pi}{\Omega_o}\frac{Ze^2\cos(qR_c)}{q^2}. \tag{4.14}$$

Figure 4.3 shows the effect of the pseudopotential on the total dielectric function for the binary alloy NbTa when the structure of an atom is considered through introducing the pseudopotential,

Figure 4.4 shows the difference between the total dielectric function with van der Waals and without van der Waals interaction. The calculation is based on equation (3.52) and includes the pseudopotential presented in equation (4.14) and the electronic dielectric function shown in figure (3.1).

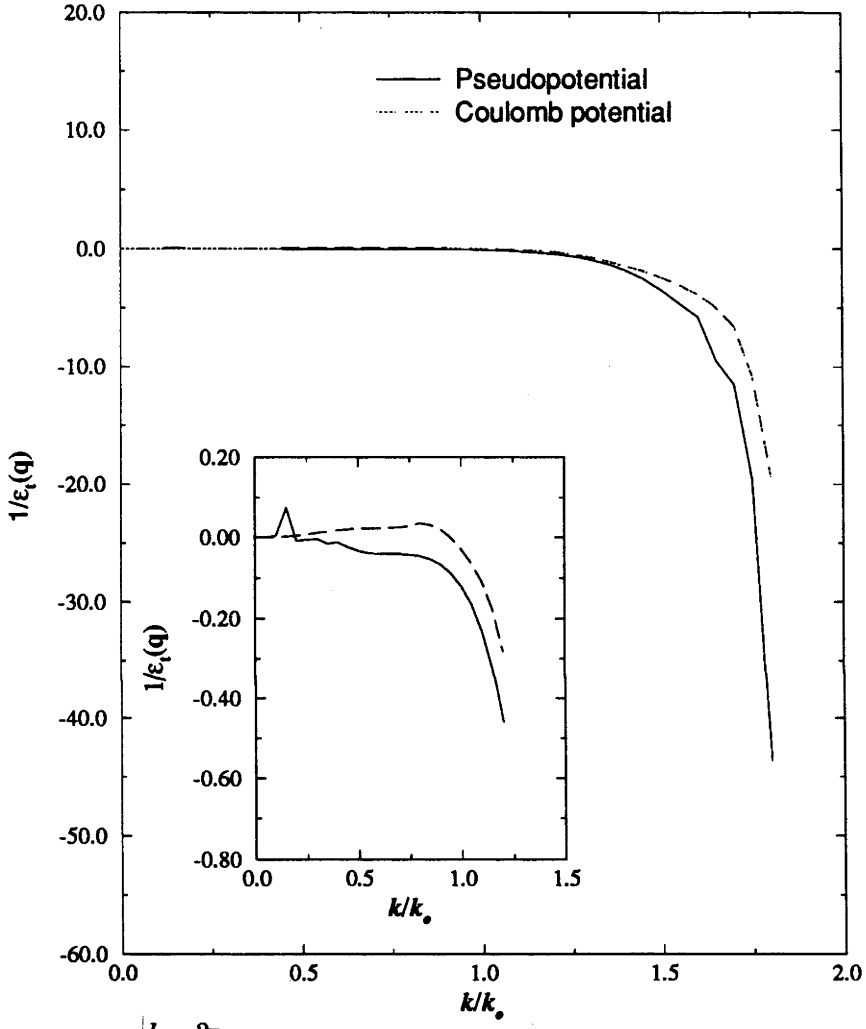

Figure 4.1: $k_0 = 2\pi/a$. **q** is along (1,0,0). The figure shows the effect of pseudopotential on the total dielectric function for aluminium

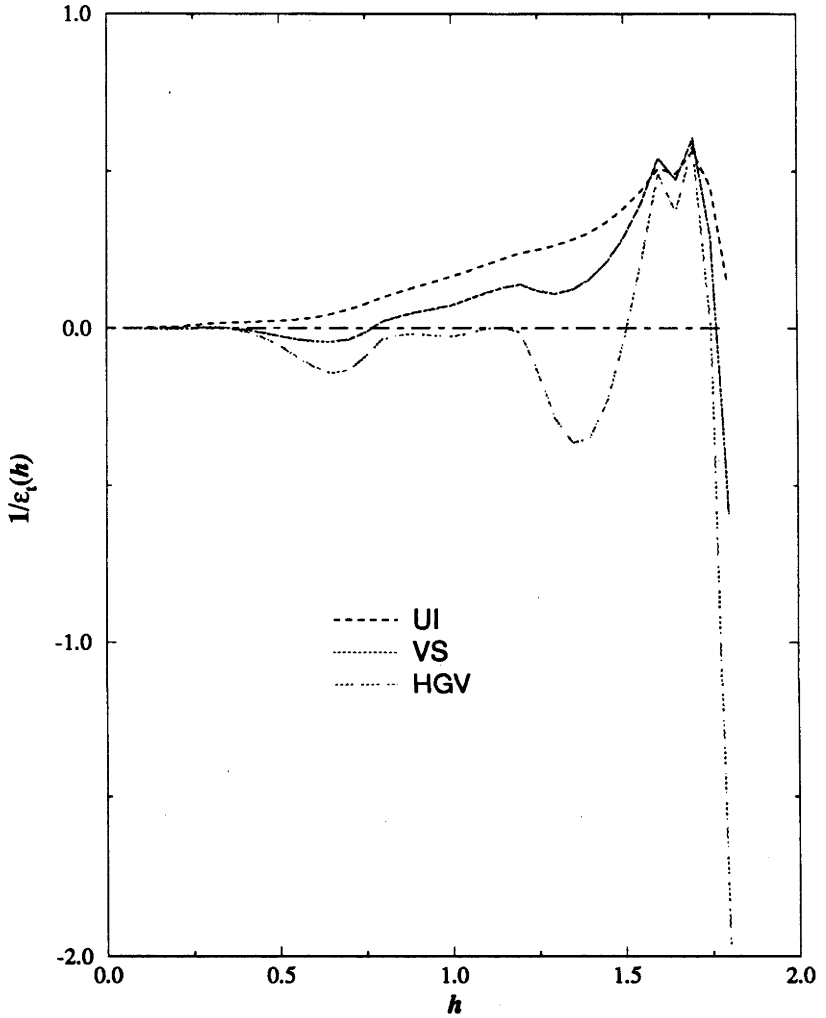

Figure 4.2: $h = q\frac{a}{2\pi}$ is along (1,0,0). Three curves represent three different case of local field correction, UI, VS and HGV.

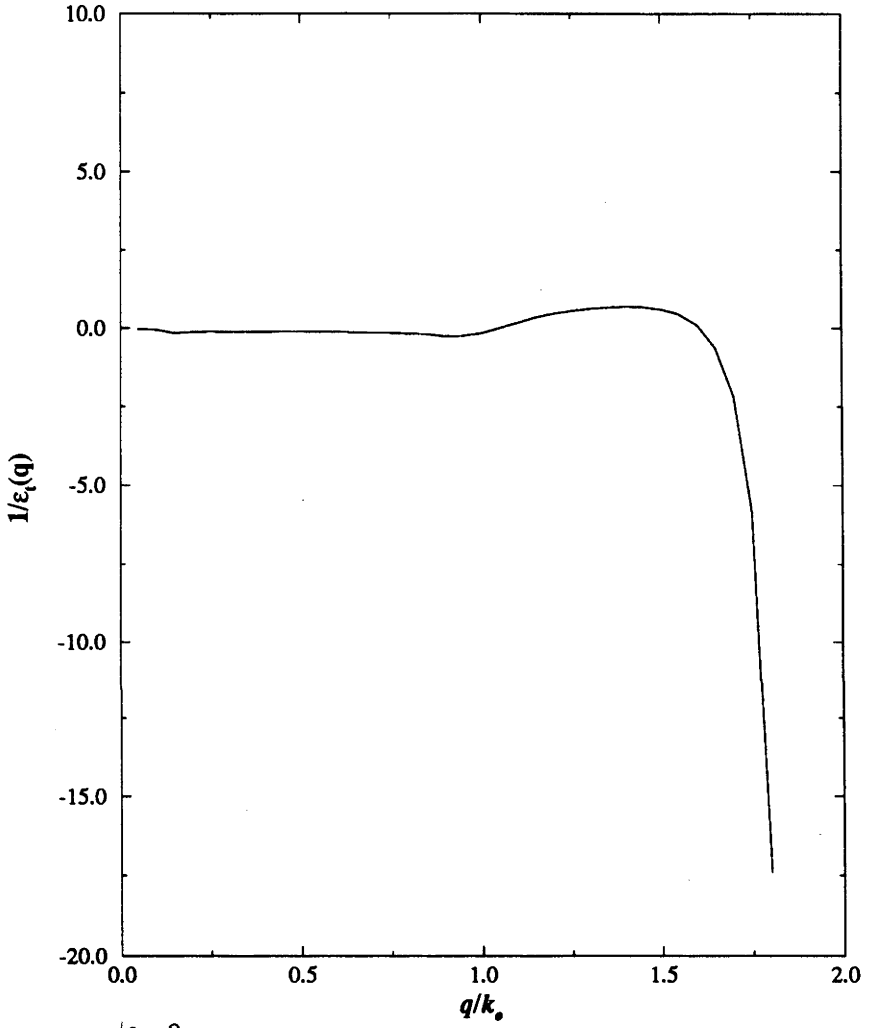

Figure 4.3: $k_0 = 2\pi/a$ is along (1,0,0). The figure shows the effect of pseudopotential on the total dielectric function for binary alloy NbTa comparison

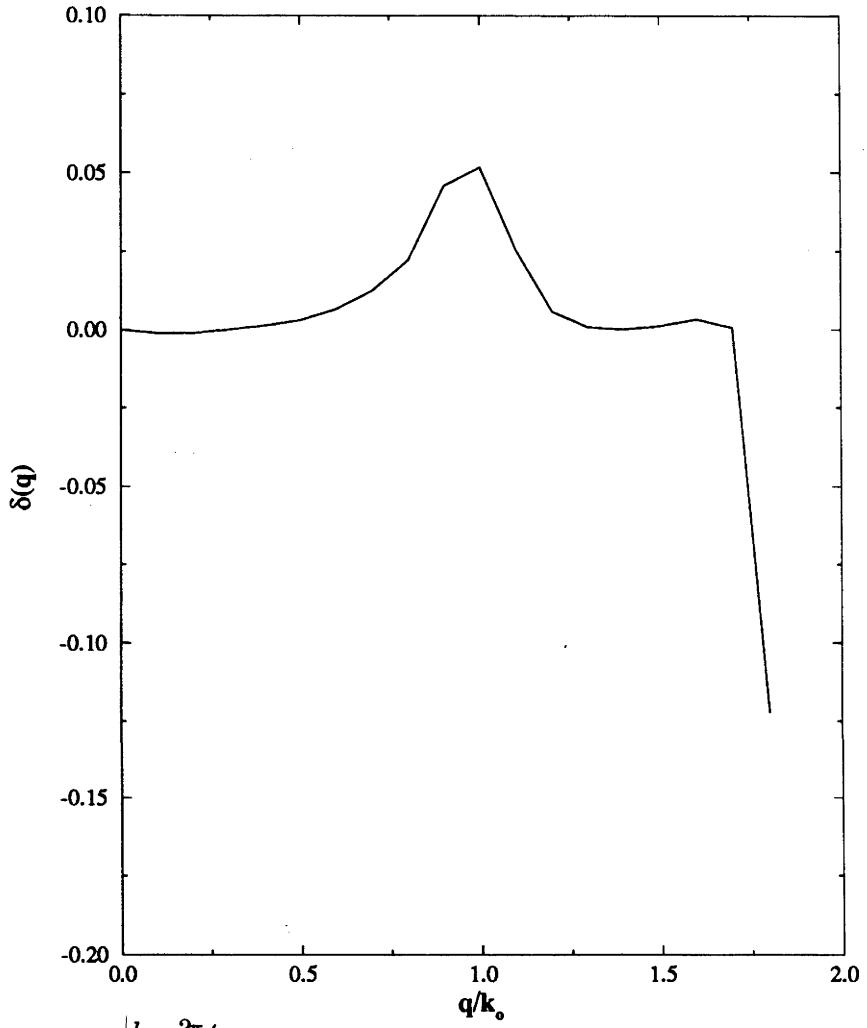

Figure 4.4: $k_0 = 2\pi/a$. $\mathbf{q}$ is along (1,0,0). $\delta(\mathbf{q}) = 1/\varepsilon_t(\mathbf{q}) - 1/\varepsilon_t'(\mathbf{q})$. $\varepsilon_t'(\mathbf{q})$ is the total dielectric function with van der Waals interaction considered. $\delta(\mathbf{q})$ is the difference between the inverse total dielectric function without van der Waals interaction and with van der Waals interaction. Both of them include the pseudopotential.

4.2 Superconducting energy gap

It is widely believed that the net attraction leading to electron pair formation in a superconductor arises from screening due to the dielectric function at zero frequency, $\varepsilon_t(\mathbf{k},0)$. The screened interaction potential is used in the calculation of the energy gap in the BCS theory of superconductivity. It has been shown [see Dolgov *et al* (1981), Dolgov and Maksimov (1982), Kirzhnits (1976) and Kirzhnits (1989)] that in the static limit, $1/\varepsilon_t(\mathbf{k},0) \leq 1$. This condition is consistent with $\varepsilon_t(\mathbf{k},0)$ being negative for some finite values of $\mathbf{k}$. At small wave vectors, however, there are some arguments about the restriction on the sign of the total dielectric function. Pines and Nozières (1966) [see also Cohen and Anderson (1972) and Martin (1967)] have stated that stability requires $\varepsilon_t(\mathbf{k},0) > 0$. But from more detailed analysis, it has been shown that the negative dielectric function satisfies the stability criterion [see Allen *et al* (1988) and Dolgov and Maksimov (1989)].

In the BCS theory of superconductivity, it has been shown that the electron-phonon interaction can lead to an instability to a normal metallic state. Due to an attractive interaction mediated by phonons, electrons on the Fermi surface can pair up [see Schrieffer (1964), de Gennes (1966), Mersevey and Schwartz (1969) and Tinkham (1975)]. An energy gap developed which is given by the following equation [see Schrieffer (1964)],

$$\Delta(\mathbf{k}) = -\frac{1}{2}\sum_{\mathbf{k}'} \frac{V_{\mathbf{k}\mathbf{k}'}\Delta(\mathbf{k}')}{\sqrt{E^2(\mathbf{k}') + \Delta^2(\mathbf{k}')}} \tag{4.15}$$

where $E(\mathbf{k}) \equiv \hbar^2(k^2 - k_F^2)/2m$ is the energy required to create a quasi-particle of momentum $\mathbf{k}$ in the superconducting state. In the BCS theory [see Bardeen *et al* (1957)], the effective interaction term $V_{\mathbf{k}\mathbf{k}'}$ is assumed to be a negative constant on a shell on the Fermi surface. It is in fact given by [see Allen *et al* (1988)]

$$V_{\mathbf{k}\mathbf{k}'} = \frac{V(\mathbf{q})}{\varepsilon_t(\mathbf{q})} + \tilde{V}(\mathbf{q}), \tag{4.16}$$

where

$$\mathbf{q} = \mathbf{k}' - \mathbf{k},$$

$V(\mathbf{q}) = 4\pi e^2/(\Omega q^2)$ is the bare Coulomb interaction in $\mathbf{q}$ - space, and $\tilde{V}(\mathbf{q})$ is vertex correction and nonlinear correction etc. [see Allen *et al* (1988)]. In this thesis, $\tilde{V}(\mathbf{q})$ is dropped considering it as a small contribution.

The relationships between the various quantities in equation (4.15) are shown in figure 4.5.

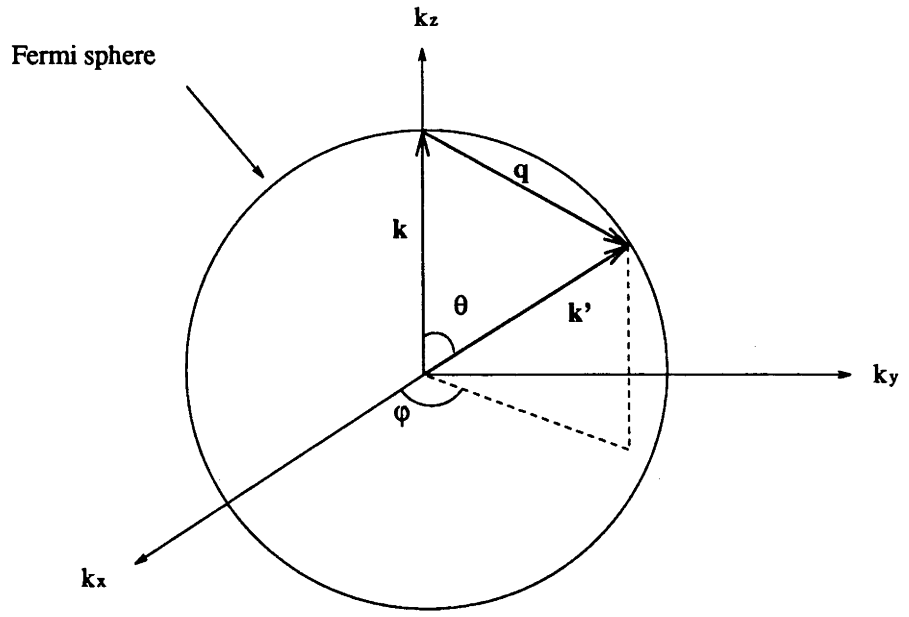

Figure 4.5: $\mathbf{k}$ is fixed and $\mathbf{k}'$ varies in the Fermi sphere. $\mathbf{q} = \mathbf{k}' - \mathbf{k}$

Near zero temperature, $|\mathbf{k}| \approx |\mathbf{k}'| \approx k_F$, therefore

$$|\mathbf{q}| = \sqrt{|\mathbf{k}|^2 + |\mathbf{k}'|^2 - 2|\mathbf{k}||\mathbf{k}'|\cos\theta}$$

$$= 2k_F \sin\frac{\theta}{2}. \tag{4.17}$$

By assuming the energy gap to be isotropic and independent of $\mathbf{k}$, $\Delta_{\mathbf{k}} = \Delta$, and by substituting equation (4.16) into equation (4.15), we obtain,

$$1 = -\frac{\Omega}{2(2\pi)^3}\int \frac{V(\mathbf{q})}{\varepsilon_t(\mathbf{q})\sqrt{E^2(\mathbf{k}) + \Delta^2}} d^3\mathbf{k}. \tag{4.18}$$

Using the relations $dE = (\hbar^2/m)kdk$ and $d^3k = k^2 dk \sin\theta d\theta d\varphi$ the above integral can be expressed as an integral over energy and angles. There is a limit for the integral which can be understood as per the following arguments, by taking the form of equation (2.49) as an example. The frequency of longitudinal acoustic phonons basically satisfies the inequality

$$\omega_L^2(\mathbf{q}) \leq \omega_D^2, \tag{4.19}$$

where ω_D is Debye frequency. Therefore in equation (2.49), a part of the second term on the right satisfies the inequality,

$$\frac{\mathbf{q}\cdot\Phi^{-1}(\mathbf{q})\cdot\mathbf{q}}{q^2} = \frac{\omega_{pl}^2}{\omega_L^2(\mathbf{q})} \geq \frac{\omega_{pl}^2}{\omega_D^2}, \tag{4.20}$$

where ω_{pl} is the ion plasma frequency. Thus

$$\frac{1}{\varepsilon_t(\mathbf{q})} = \frac{1}{\varepsilon_e(\mathbf{q})} - \frac{1}{\varepsilon_e^2(\mathbf{q})}\frac{\mathbf{q}\cdot\Phi^{-1}(\mathbf{q})\cdot\mathbf{q}}{q^2} \leq \frac{1}{\varepsilon_e(\mathbf{q})} - \frac{\omega_{pl}^2}{\varepsilon_e^2(\mathbf{q})\omega_D^2}. \tag{4.21}$$

The interaction between a pair of electrons in superconductivity is screened by a total dielectric function which is not the static one of equation (4.21). It has a form that takes into account of processes such as scattering of the pair with momenta $(\mathbf{k}, -\mathbf{k})$ to momenta $(\mathbf{k}', -\mathbf{k}')$ with exchange of a phonon with wave number $\mathbf{q} = \mathbf{k}' - \mathbf{k}$. A simple way of approximately taking this into consideration is to replace in equation (4.21) the term $\frac{\mathbf{q}\cdot\Phi^{-1}(\mathbf{q})\cdot\mathbf{q}}{q^2}$ by $\frac{\mathbf{q}\cdot\Phi^{-1}(\mathbf{q},\omega)\cdot\mathbf{q}}{q^2}$ where $\omega = \epsilon/\hbar$, ϵ is the change of energy of the pair in the scattering process. An estimate of the last expression is

$$\frac{\mathbf{q}\cdot\Phi^{-1}(\mathbf{q},\omega)\cdot\mathbf{q}}{q^2} \sim \frac{\omega_{pl}^2}{\omega_L^2(\mathbf{q}) - (\epsilon/\hbar)^2} \geq \frac{\omega_{pl}^2}{\omega_D^2 - (\epsilon/\hbar)^2} \tag{4.22}$$

This was arrived at by considering the dynamics at zero frequency, and then estimating the second order correction due to finite ω. Note the similarity between this

equation and that calculated by Cohen and Anderson (1972) using the Bardeen-Pines phonon-induced interaction [Cohen and Anderson (1972)]. From equation (4.22) and (4.21) it is seen that attractive interaction between an electron pair is possible only if $\omega < \omega_D$. This implies that the limits of the energy integration in (4.18) are from $-\hbar\omega_D$ to $\hbar\omega_D$.

Now, following the procedure stated after (4.18) and with the above arguments for the limits of the integral equation, (4.18) becomes

$$1 = -\frac{\Omega k_F m}{2(2\pi)^3\hbar^2}\int_{-\hbar\omega_D}^{\hbar\omega_D}\frac{dE}{\sqrt{E^2+\Delta^2}}\int\frac{V(\mathbf{q})}{\varepsilon_t(\mathbf{q})}\sin\theta d\theta d\varphi. \tag{4.23}$$

By solving equation (4.23), The energy gap then is given by

$$\Delta = \frac{\hbar\omega_D}{|\sinh(1/2z)|}, \tag{4.24}$$

where

$$z = \frac{\Omega k_F m}{2(2\pi)^3\hbar^2}\int\frac{V(\mathbf{q})}{\varepsilon_t(\mathbf{q})}\sin\theta d\theta d\varphi. \tag{4.25}$$

the quantities k_F, Fermi wave vector, n, electron density and the inter-electronic separation, r_s are related through the following equation,

$$k_F = (3\pi^2 n)^{\frac{1}{3}} = (\frac{9\pi}{4})^{\frac{1}{3}}/r_s a_o \tag{4.26}$$

4.3 Results and discussion

The results for the energy gap of aluminium and the binary alloy NbTa are presented in this section. In the BCS theory, the magnitude of the energy gap $\Delta(0)$ (at absolute zero temperature) depends on the strength of the electron-phonon coupling λ. This dependence has the following form:

$$\Delta(0) = 2\hbar\Theta e^{-1/\lambda} \tag{4.27}$$

where $\Theta \sim \Theta_D$, the Debye frequency [see Ashcroft and Mermin (1976) and Kresin

and Wolf (1990)]

The energy gap $\Delta(T)$ decreases with increasing temperature. At the critical temperature the energy gap vanishes and the material becomes normal. The critical temperature is described by the following fundamental expression,

$$k_B T_c = 1.14\hbar\Theta e^{-1/\lambda} \tag{4.28}$$

where $\Theta \sim \Theta_D$.

Therefor the ratio of (4.27) and (4.28) gives a formula independent of the phenomenological parameter λ:

$$\frac{2\Delta}{k_B T_c} = 3.5 \tag{4.29}$$

4.3.1 Results for aluminium

Energy gaps are calculated in this section by two different methods. One is from the prediction of the BCS theory which is shown in equation (4.29), and other is based on equation (4.24) considering all the physical factors in the calculation of the energy gap such as the local-field correction, the total dielectric function and the ion-electron pseudopotentials.

For aluminium, $r_s = 2.07$. Through the equation (4.26), k_F is obtained as $k_F = 1.75(\text{Å}^{-1})$. The lattice constant of aluminium is $a = 4.05(\text{Å})$. Substituting the total dielectric function for aluminium which is shown in figure 4.1 into (4.24) and taking the HGV local field correction into consideration, the energy gap can be calculated and shown

$$\Delta^{Al}_{c(HGV)} = 0.949 \times 10^{-3}\hbar\omega_D, \tag{4.30}$$

where the subscript c denotes the energy gap which is calculated by the formula developed in this thesis.

When the VS local field correction function is taken the result is much less than the real value (see below). With UI local field correction function, the energy gap

is around $4.25 \times 10^{-5}\hbar\omega_D$ which is far too small.

If the van der Waals interaction between ions is considered, the energy gap which took the HGV local-field correction into consideration becomes,

$$\Delta^{Al}_{cv(HGV)} = 1.041 \times 10^{-3}\hbar\omega_D, \tag{4.31}$$

where v represents the value calculated due to the van der Waals interaction.

There is a difference between the results produced by the calculation above and the predicted results of BCS theory. The difference is mainly due to the electronic dielectric function the form of which is not known exactly. This can be seen in the insert in figure 4.6, where differences in local field corrections lead to different form for $1/\varepsilon_e(q)$. The gap depends rather sensitively on the chosen form of $\varepsilon_e(q)$. In figure 4.6 the dot-dashed line is the electronic dielectric function with HGV local field correction, and the value of the corresponding gap is in equation (4.31). The solid line is a slight adjustment in the value of the electronic dielectric function, and even this slight adjustment gives a much improved value of the gap, bringing it closer to the BCS prediction. The adjustment was done empirically, with many trials with assumed numerical forms for $1/\varepsilon_e(q)$.

The superconducting energy gaps with and without van der Waals interaction calculated with this adjusted electronic dielectric function which gives,

$$\Delta^{Al}_{c} = 4.52 \times 10^{-3}\hbar\omega_D \tag{4.32a}$$

$$\Delta^{Al}_{cv} = 4.83 \times 10^{-3}\hbar\omega_D. \tag{4.32b}$$

It is thus seen that inclusion of the van der Waals interaction increases the calculated energy gap by about a 6.8% over the value in (4.32a).

In the prediction of the BCS theory, the superconducting energy gap is calculated by the formula [see Ashcroft and Mermin (1976) and Gupta (1991)]

$$\Delta^{Al} = \frac{3.5}{2} k_B T_c \tag{4.33}$$

where T_c is transition temperature and k_B is Boltzman's constant. For aluminium the transition temperature and Debye temperature are [see McMillan (1968) and Kittel (1976)],

$$\begin{aligned} T_c &= 1.140\text{K} \\ \Theta_D &= 428\text{K}. \end{aligned}$$

Therefore the energy gap of aluminium through formula (4.33) is

$$\Delta^{Al} = 4.65 \times 10^{-3} \hbar\omega_D. \tag{4.34}$$

For convenience of discussion later, the data of energy gap (in units of $\hbar\omega_D$) for aluminium calculated by various local field functions are listed in the following table. Δ_c and Δ_{cv} have been calculated using the adjusted form of $1/\varepsilon_e(q)$ which is shown in figure 4.6.

$\Delta_{c(HGV)}$	0.95×10^{-3}
$\Delta_{c(VS)}$	0
$\Delta_{c(UI)}$	4.25×10^{-5}
$\Delta_{cv(HGV)}$	1.04×10^{-3}
Δ_c	4.52×10^{-3}
Δ_{cv}	4.83×10^{-3}
$\Delta_{\text{BCS(predicted)}}$	4.65×10^{-3}

4.3.2 Results for the binary alloy NbTa

Here the binary alloy of NbTa with equal concentration of Nb and Ta is considered. The energy gaps of binary alloy NbTa are calculated by two different methods

as in §4.3.1 The r_s value for this alloy is 1.796 which gives $k_F = 2.02(\text{Å}^{-1})$. The lattice constant for NbTa is taken as $a = 3.3(\text{Å})$. Including the local field correction and the pseudopotential in the total dielectric function which is calculated in the thesis and shown in figure 4.3, the energy gap is obtained as

$$\Delta_c = 0.1030\hbar\omega_D. \tag{4.35}$$

When the van der Waals interaction between ions is included the energy gap of NbTa is

$$\Delta_{cv} = 0.0982\hbar\omega_D. \tag{4.36}$$

It is seen that the value of energy gap Δ of the alloy NbTa is decreased by 5% when van der Waals interaction is included. The calculated value is twice as large as the BCS predicted value which is obtained as follows.

For a binary alloy, a formula to calculate the ratio T_c/Θ_D is given by

$$\left[\ln(\frac{T_c}{\Theta_D})\right]^{-1}_{AB} = C_A\left[\ln(\frac{T_c}{\Theta_D})\right]^{-1}_{A} + C_B\left[\ln(\frac{T_c}{\Theta_D})\right]^{-1}_{B} \tag{4.37}$$

where A, B refer to the atomic species in the alloy, and C_A and C_B are their concentrations which are taken 50% each in this thesis (see Vonsovsky *et al* 1977). This formula is used for the NbTa alloy to calculate the ratio T_c/Θ_D and hence energy gap Δ. This value of Δ is compared with the results calculated from the total dielectric function.

The data on transition temperature and Debye temperature of Nb and Ta are [Kittel (1976)].

$$\text{N}b: \begin{cases} T_c &= 9.5\text{K} \\ \Theta_D &= 275\text{K}, \end{cases}$$

and

$$\text{T}a: \begin{cases} T_c &= 4.483\text{K} \\ \Theta_D &= 240\text{K}. \end{cases}$$

Therefore the ratio of the T_c/Θ_D of binary alloy NbTa can be obtained through formula (4.37)

$$\frac{T_c}{\Theta_D} = 0.025955. \tag{4.38}$$

Substituting the above value of the T_c/Θ_D in the expression for the BCS gap function, gives

$$\Delta = \frac{3.5}{2}\frac{T_c}{\Theta_D}\hbar\omega_D = 0.0454\hbar\omega_D. \tag{4.39}$$

The energy gap (in units of $\hbar\omega_D$) of the binary alloy NbTa is tabulated below for comparison.

Δ_c	0.1030
Δ_{cv}	0.0982
$\Delta_{\text{BCS(predicted)}}$	0.0454

The difference between the calculated and predicted results will be discussed in the next section.

4.3.3 Discussions

The results in the previous subsections show that there are substantial differences between theoretical results and the predicted results from the BCS theory on the basis of equation (4.33).

The reasons for the discrepancies include:

1. Local-field function

The total dielectric function of the electron gas is a very sensitive function to the local field correction. This point can be seen from the figure 4.2. So far there is no agreed form of the electronic local-field function. Many approximations have been made for the local field correction to achieve good agreement with different

physical quantities [see Gorobchenko *et al* (1989), Brovman and Kagan (1974) and Allen *et al* (1988)], but no such attempt has been made to give a good value of the total dielectric function.

2. Pseudopotential

The effect of the chosen form of the pseudopotential on the total dielectric function is as sensitive as the chosen form of the local field correction. The forms used in the thesis for the calculation are not necessarily the best choice. There are many approximations in the form of the pseudopotentials in metals, [see Harrison (1966), Heine (1970), Cohen and Heine (1970) and Yastrebov and Katsnelson (1987)], and it is possible that a properly chosen form would provide better agreement for Δ than what I have used.

In the calculation of the binary alloy NbTa, the simplest form of pseudopotential is used. Within this pseudopotential form, an atomic radius R_c is used as an approximation which is taken from *Handbook of Atomic Data* [see Fraga et al (1976)]. There would be some difference if a proper radius R used.

3. Anharmonicity

The harmonic approximation for the dynamic matrix is used in the discussion of aluminium in §4.1. Brovman and Kagan (1974) has shown that if the third order anhomonicity is taken into consideration, the phonon dispersion curves in aluminium becomes much closer to the experimental results. This implies that consideration of anharmonicity may improve the total dielectric function and the energy gap.

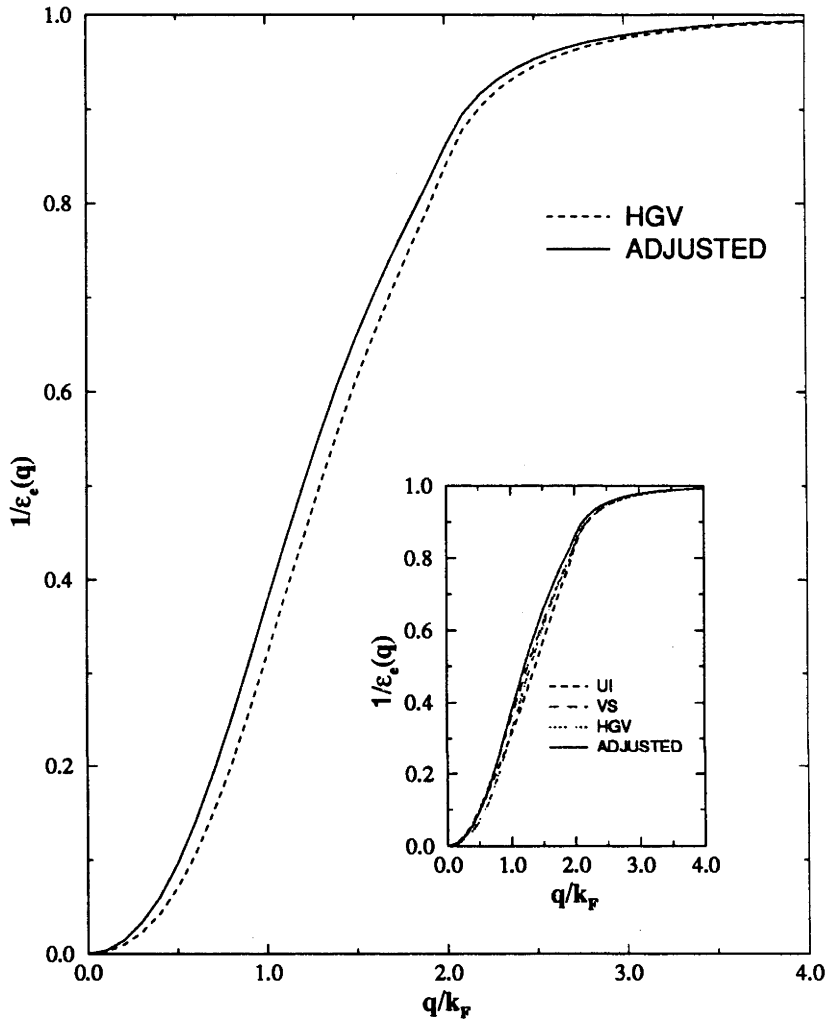

Figure 4.6: The dot-dashed line represents the curve of electronic dielectric function by considering the HGV local field correction. The solid line represents the chosen form of the electronic dielectric function, that gives the energy gap in equation (4.32). The insert gives the form of $1/\varepsilon_e(q)$ with different local field corrections, and shows the chosen form of $1/\varepsilon_e(q)$ for the present calculation in relation to the other forms.

CHAPTER 5

Conclusion

5.1 Brief summary

The main purpose of this thesis is to develop a general theory of total dielectric function of a metallic solid from first principles, taking into account van der Waals interaction between ions, in addition to electron-ion interactions. As an application of this total dielectric function, superconducting energy gaps are calculated in the simple metal, aluminium, and the binary alloy, NbTa.

The basic idea of electronic dielectric and total dielectric function developed was presented in chapter 1, emphasising its physical origin. The total dielectric function for a simple metal was studied in Chapter 2. When considering the total dielectric function in the general case, in the medium range of values of the wave number $\mathbf{k}$, a concept of local-field correction in the electronic system is brought to the discussion. With these, a formula for the total dielectric function of metal is obtained quite satisfactorily.

In Chapter 3, the total dielectric function of an alloy is discussed. The total dielectric function for multi component plasma is developed from first principles. In the medium range of values of $\mathbf{k}$, the total dielectric function of a binary alloy system is obtained. With this total dielectric function, the binary alloy NbTa is discussed. Since Nb and Ta are transition metals, the interaction between electrons and ions involves pseudopotentials.

As mentioned in Chapter 4, there are different statements concerning the sign of total dielectric function near the origin in reciprocal space. Allen *et al* (1988) claimed that the $\varepsilon_t(\mathbf{k}, 0)$ can be negative because the creation of a spontaneous

charge fluctuation should include not only the Coulomb energy but quantum-mechanical effects such as the change in kinetic energy as well [see Allen *et al* (1988)]. Dolgov and Maksimov (1989) claimed that for metals the total dielectric function may remain negative at as small values of $\mathbf{q}$ as desired except at the isolated point $\mathbf{q} = 0$ where $\varepsilon_t(0,0) \geq 1$. This negative value is caused due to the local-field correction. The total dielectric functions which are obtained in this thesis confirm the statement of Dolgov and Maksimov (1989).

In Chapter 4, the superconducting energy gaps are evaluated by using the total dielectric function developed in Chapter 2 and 3. And the total dielectric functions are calculated again taking pseudopotentials into account. The results are reasonably good and van der Waals interaction brings noticeable improvements. The differences between the results predicted from BCS theory and that evaluated by considering the total dielectric functions from Chapter 2 and 3 can be understood by considering all the approximations. It has been tested that if some parameters for electronic dielectric function are changed slightly, the results can be changed dramatically. It does not mean that the electronic dielectric function involved is arbitrary, but an electronic dielectric function with a proper local-field corrections needs to be carefully developed. Another point which should be brought to attention is the form of the pseudopotential, when discussing transition metals in particular. The structure of the atom of a transition metal can not be simply ignored when considering the interaction between electrons and ions. The form of the pseudopotential plays very important role in the calculated value of the total dielectric function, as can be seen in figure 4.3. The pseudopotential used to calculate the total dielectric function for the binary alloy NbTa in the thesis is the simplest model potential [see Heine (1970)]. This model does not take into account the details of the structure of atoms for transition metals. Pseudopotentials for transition metals have not been well developed. The reason is the theory of pseudopotential for transition and rare-earth metals is rather complicated where relatively tightly bound d and/or f electrons play important roles.

The other important factor to improve the results is the consideration of the third order anharmonic corrections to dynamical matrix. Brovman and Kagan

(1974) have discussed this effect in their study of phonon dispersion.

5.2 Future directions

There are many applications of the total dielectric function. I have confined to an application to the theory of superconductivity, which has remained a highly active subject.

The theory of superconductivity requires a net attractive interaction between electrons near Fermi surface. In BCS theory, in a low T_c superconductor, it is believed that the electrons near Fermi surface effectively attract each other to form bound pair, and their binding energy gives the energy gap. Though the direct electrostatic interaction between a pair of electrons is repulsive, it has been shown, by experimental and theoretical analysis that the ionic motion can overscreen the Coulomb interaction, leading to a net attraction. The cause of the attraction thus the screening, and this can be calculated through the total dielectric function which is evaluated in the Chapters 2 and 3. The experimental fact of the isotope effect is direct evidence that the ionic motion plays a role in establishing superconductivity. The fact that there is any dependence of T_c on the ionic mass demonstrates that the ions cannot play a merely static role in the transition, but must be dynamically involved. The theoretical possibility has been shown by many people [see for example Crisan (1989)]. In Chapter 2 and 4, a simplified model has been used, that allows the ions to move in response to the motions of the electrons, and that leads to a net interaction between a pair of electrons with wave vectors $\mathbf{k}$ and $\mathbf{k}'$, of the form

$$V_{\text{eff}}(\mathbf{k},\mathbf{k}') = \frac{4\pi e^2}{q^2 \varepsilon_t(\mathbf{q})}; \tag{5.1}$$

where $\mathbf{q} = \mathbf{k}' - \mathbf{k}$.

Therefore overscreening by the ionic motion can yield a net attractive interaction between electrons with energies sufficiently close together. This attraction underlies the theory of superconductivity. Theoretically, any other mechanism leading to a net attractive interaction between electrons near Fermi surface would also

lead to a superconducting state at low enough temperature. However, no case of superconductivity due to other mechanism have been convincingly established in metals [see page 740, Ashcroft and Mermin (1976)]. The situation is much more complicated now with the advent of high T_c superconductivity.

We need to understand better (i) the dielectric response of the conduction electrons in the system including local field corrections, and (ii) the nature of the electron-ion interaction, to improve upon the treatment I have followed in this thesis.

APPENDIX A

Fourier relations of some physical quantities in lattices

The Fourier expansion of a function of $\mathbf{r}$ with lattice periodicity (i.e.) $f(\mathbf{r}+\mathbf{R}_l) = f(\mathbf{r})$, where $\mathbf{R}_l$ is a lattice vector has been discussed in detail in many standard texts [see for instance Ziman (1965)]. Here the main points are summarised. The Fourier expansion of such a function $f(\mathbf{r})$ is

$$f(\mathbf{r}) = \sum_{\mathbf{k}} g(\mathbf{k}) e^{i\mathbf{r}\cdot\mathbf{k}}. \tag{A.1}$$

When looking at the space dependence of the displacements in the normal modes,

$$\mathbf{q}_{\mathbf{k}} = \sum_{l} \mathbf{u}_l \exp(-i\mathbf{k}\cdot\mathbf{R}_l), \tag{A.2}$$

it can be seen immediately that not all $\mathbf{k}$ vectors are independent; in fact $\mathbf{k}$ is completely equivalent to all other vectors formed by adding a vector of the "reciprocal lattice" $\mathbf{K}_n$; thus

$$\mathbf{k} \longleftrightarrow \mathbf{k} + \mathbf{K}_n. \tag{A.3}$$

where

$$\mathbf{K}_n \cdot \mathbf{R}_l = 2\pi p. \tag{A.4}$$

p is an integer. All the $\mathbf{l}$ and $\mathbf{K}_n$ vectors can be expressed as a linear combination of the three basic lattice vectors in real space and reciprocal space a_σ and b_σ, $\sigma \in \{1,2,3\}$, respectively,

$$\mathbf{R}_l = l_1\mathbf{a}_1 + l_2\mathbf{a}_2 + l_3\mathbf{a}_3 \qquad l_1, l_2, l_3 \text{ integers.} \tag{A.5}$$

and

$$\mathbf{K}_n = n_1\mathbf{b}_1 + n_2\mathbf{b}_2 + n_3\mathbf{b}_3 \qquad n_1, n_2, n_3 \text{ integers} \tag{A.6}$$

where

$$\mathbf{b}_1 = 2\pi\frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_2 = 2\pi\frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \quad \text{and} \quad \mathbf{b}_3 = 2\pi\frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \tag{A.7}$$

which we can write more compactly as

$$\mathbf{b}_\lambda \cdot \mathbf{a}_\sigma = 2\pi\delta_{\lambda\sigma} \qquad \lambda, \sigma \in \{1, 2, 3\}. \tag{A.8}$$

If the number of atoms N in a system with volume Ω is very large, the following orthogonality relation holds:

$$\sum_n e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_n} = N\delta_{\mathbf{k},\mathbf{k}'+\mathbf{K}_n}. \tag{A.9}$$

For a normal mode $\mathbf{q}_\mathbf{k}$, the relation between displacements $\mathbf{u}_i$ from equilibrium in real space must be of the form

$$\mathbf{u}_{i+1} = e^{i\mathbf{k}\cdot\mathbf{a}}\mathbf{u}_i, \tag{A.10}$$

where the lattice points are separated by the elementary lattice vector $\mathbf{a}$. Then at each lattice point,

$$\mathbf{u}_i = \mathbf{q}_\mathbf{k} e^{i\mathbf{k}\cdot\mathbf{R}_i}, \tag{A.11}$$

where $\mathbf{R}_i$ is the vector of the ith lattice point.

For a general motion of the lattice, the vibrations can be expanded in normal modes.

$$\mathbf{u}_i = \frac{1}{N}\sum_{\mathbf{k}\in\mathbf{K}_1} \mathbf{q}_k e^{i\mathbf{k}\cdot\mathbf{R}_i}. \tag{A.12}$$

$$\ddot{\mathbf{u}}_i = \frac{1}{N}\sum_{\mathbf{k}\in\mathbf{K}_1} \ddot{\mathbf{q}}_k e^{i\mathbf{k}\cdot\mathbf{R}_i}, \tag{A.13}$$

The $\mathbf{k}$ is restricted in $\mathbf{K}_1$ because of the periodicity in the ionic system. A list of formulae which are used in thesis are given below,

$$\frac{1}{|\mathbf{R}_i - \mathbf{r}|} = \frac{4\pi}{\Omega} \sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{r})}}{k^2}. \tag{A.14}$$

$$\nabla \frac{1}{|\mathbf{R}_i - \mathbf{r}|} = \frac{4\pi}{\Omega} \sum_{\mathbf{k}} i\mathbf{k} \frac{e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{r})}}{k^2}. \tag{A.15}$$

$$\delta(\mathbf{r} - \mathbf{R}_i) = \frac{1}{\Omega} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{r})}. \tag{A.16}$$

$$\nabla\delta(\mathbf{r} - \mathbf{R}_i) = \frac{1}{\Omega} \sum_{\mathbf{k}} i\mathbf{k} e^{i\mathbf{k}\cdot(\mathbf{R}_i - \mathbf{r})}. \tag{A.17}$$

$$n(\mathbf{r}, t) = \frac{1}{\Omega} \sum_{\mathbf{k}} n(\mathbf{k}, t) e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{A.18}$$

$$n(\mathbf{k}, t) = \int_{\Omega} n(\mathbf{r}, t) e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r. \tag{A.19}$$

$$\sum_{\mathbf{k}} (...) = \frac{\Omega}{(2\pi)^3} \int (...) d^3k. \tag{A.20}$$

APPENDIX B

The Response Function $\chi_e(\mathbf{k},\omega)$

This appendix is to show what should be the form of $\chi_e(\mathbf{r}-\mathbf{r}',t)$ in reciprocal space. For simplicity, taking $\rho_{ext}(\mathbf{k},\omega)=0$ (since this will not affect the general results) equation (2.11) becomes

$$-en(\mathbf{k},\omega)=(\frac{1}{\varepsilon_e(\mathbf{k},\omega)}-1)\rho(\mathbf{k},\omega), \tag{B.1}$$

and in a homogeneous medium,

$$-en(\mathbf{r},t)=\int_\Omega \chi_e(\mathbf{r}-\mathbf{r}',t-t')\rho(\mathbf{r}',t')d^3r'dt'. \tag{B.2}$$

The Fourier series of $n(\mathbf{r})$ and $\rho_{ion}(\mathbf{r})$ are respectively,

$$n(\mathbf{r})=\frac{1}{\Omega}\sum_{\mathbf{k}} n(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}} \tag{B.3}$$

and

$$\rho(\mathbf{r})=\frac{1}{\Omega}\sum_{\mathbf{k}} \rho(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{B.4}$$

Suppose $\chi_e(\mathbf{r}-\mathbf{r}')$ is well behaved so that it may be expanded it in a Fourier series,

$$\chi_e(\mathbf{r}-\mathbf{r}')=\frac{1}{\Omega}\sum_{\mathbf{k}} \chi_e(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}. \tag{B.5}$$

If concerning to time t, equation (B.3) and (B.4) are respectively,

$$n(\mathbf{r},t)=\frac{1}{2\pi\Omega}\int_{-\infty}^{\infty}\sum_{\mathbf{k}} n(\mathbf{k},\omega)e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega t}d\omega, \tag{B.6}$$

and

$$\rho(\mathbf{r},t) = \frac{1}{2\pi\Omega}\int_{-\infty}^{\infty}\sum_{\mathbf{k}}\rho(\mathbf{k},\omega)e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega t}d\omega. \tag{B.7}$$

Now using the Fourier series (B.5), the above two equations may be reduced to

$$-\frac{e}{2\pi\Omega}\int_{-\infty}^{\infty}\sum_{\mathbf{k}}n(\mathbf{k},\omega)e^{i\mathbf{k}\cdot\mathbf{r}}e^{-i\omega t}d\omega$$

$$= \frac{1}{2\pi\Omega}\int_{-\infty}^{t}\int_{\Omega}\sum_{\mathbf{k}}\chi_e(\mathbf{k},t-t')e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\rho(\mathbf{r}',t')d\mathbf{r}'dt'. \tag{B.8}$$

The response function is defined as

$$\chi_e(\mathbf{k},t) = \begin{cases} 0 & \text{if } t<0 \\ \chi_e(\mathbf{k},t) & \text{otherwise,} \end{cases}$$

and its Fourier representation is,

$$\chi_e(\mathbf{k},t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)e^{i\omega(t)}d\omega \tag{B.9}$$

Substituting equation (B.9) in equation (B.8), gives

$$-e\int_{-\infty}^{\infty}n(\mathbf{k},\omega)e^{-i\omega t}d\omega = \frac{1}{2\pi}\int_{-\infty}^{\infty}dt'\rho(\mathbf{k},t')\frac{1}{2\pi}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)e^{-i\omega(t-t')}d\omega$$

$$= \int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)\rho(\mathbf{k},\omega)e^{-i\omega t}d\omega. \tag{B.10}$$

Therefore

$$-en(\mathbf{k},\omega) = \chi_e(\mathbf{k},\omega)\rho(\mathbf{k},\omega) \tag{B.11}$$

Comparing equation (B.1), $\chi_e(\mathbf{k},\omega)$ can be written as

$$\chi_e(\mathbf{k},\omega) = \frac{1}{\varepsilon_e(\mathbf{k},\omega)} - 1. \tag{B.12}$$

APPENDIX C

Interaction between Electrons and Ions

Suppose W_{ie} is the total potential energy of electron-ion interaction in a binary alloy system having a form:

$$W_{ie} = -e \sum_{\alpha} \sum_{j=1}^{N_\alpha} \int_{\Omega} Z_\alpha e n_e(\mathbf{r}, t) V^{ie}(\mathbf{r} - \mathbf{R}_{\alpha j}) d^3 r. \tag{C.1}$$

The force on the i-th ion of α species from the electrons in the binary alloy system will then depend on $-\nabla_{\alpha i} W_{ie}$

$$-\nabla_{\alpha i} W_{ie} = \nabla_{\alpha i} \sum_{\beta} Z_\beta e^2 \sum_{j}^{N_\beta} \int_{\Omega} n_e(\mathbf{r}, t) V^{ie}(\mathbf{r} - \mathbf{R}_{\beta j}) d^3 r. \tag{C.2}$$

From equation (3.10), $n_e(\mathbf{r}, t)$ can be written as

$$\begin{aligned} n_e(\mathbf{r}, t) &= -\sum_{\alpha i} Z_\alpha \int_{-\infty}^{t} \chi_e(\mathbf{r} - \mathbf{R}_{\alpha i}, t - t') dt' \\ &\quad -\frac{1}{e} \int_{\Omega} \int_{-\infty}^{t} \chi_e(\mathbf{r} - \mathbf{r}', t - t') \rho_{ext}(\mathbf{r}', t') d^3 r' dt'. \end{aligned} \tag{C.3}$$

Therefore,

$$\nabla_{\alpha i} \sum_{\beta} Z_\beta e^2 \sum_{j}^{N_\beta} \int_{\Omega} n_e(\mathbf{r}, t) V^{ie}(\mathbf{r} - \mathbf{R}_{\beta j}) d^3 r =$$

$$-\frac{1}{2} e^2 \nabla_{\alpha j} \sum_{\beta i}^{N_\beta} Z_\beta \int_{\Omega} \left[\sum_{\gamma l}^{N_\gamma} Z_\gamma \int_{-\infty}^{t} \chi_e(\mathbf{r} - \mathbf{R}_{\gamma l}, t - t') dt' \right] V^{ie}(\mathbf{r} - \mathbf{R}_{\beta j}) d^3 r$$

$$-e \nabla_{\alpha j} \sum_{\beta i}^{N_\beta} Z_\beta \int_{\Omega} \left[\int_{\Omega} \int_{-\infty}^{t} \chi_e(\mathbf{r} - \mathbf{r}', t - t') \rho_{ext}(\mathbf{r}', t') d^3 r' dt' \right] V^{ie}(\mathbf{r} - \mathbf{R}_{\beta j}) d^3 r$$

$$= [\mathbf{1}] + [\mathbf{2}]. \tag{C.4}$$

The factor $\frac{1}{2}$ introduced is the correction for the double counting. The first part of (C.4) is

$$[\mathbf{1}] = -\frac{1}{2}e^2\nabla_{\alpha j}\sum_{\beta i}^{N_\beta} Z_\beta \int_\Omega \left[\sum_{\gamma l}^{N_\gamma} Z_\gamma \int_{-\infty}^{t} \chi_e(\mathbf{r}-\mathbf{R}_{\gamma l}, t-t')dt'\right] V^{ie}(\mathbf{r}-\mathbf{R}_{\beta j})d^3r$$

$$= -\frac{e^2}{2\Omega^2}\nabla_{\alpha j}\sum_{\beta j\gamma l}^{N_\beta N_\gamma} Z_\beta Z_\gamma \int_\Omega \int_{-\infty}^{t} \sum_{\mathbf{k}\mathbf{k}'} \chi_e(\mathbf{k}, t-t')V^{ie}(\mathbf{k}')d^3r dt' e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{R}_{\beta j})}e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_{\gamma j})}$$

$$= -\frac{e^2}{2\Omega}\nabla_{\alpha j}\sum_{\beta j\gamma l}^{N_\beta N_\gamma} Z_\beta Z_\gamma \int_{-\infty}^{t} \sum_{\mathbf{k}} \chi_e(\mathbf{k}, t-t')V^{ie}(\mathbf{k})dt' e^{-i\mathbf{k}\cdot(\mathbf{R}_{\gamma l}-\mathbf{R}_{\beta j})}$$

$$= -\frac{e^2}{2\Omega}\nabla_{\alpha j}\sum_{\beta j\gamma l}^{N_\beta N_\gamma} Z_\beta Z_\gamma \int_{-\infty}^{t} \sum_{\mathbf{k}} \chi_e(\mathbf{k}, t-t')V^{ie}(\mathbf{k})dt' e^{-i\mathbf{k}\cdot(\mathbf{R}_{\gamma l}-\mathbf{R}_{\beta j})}$$

$$\times [(\mathbf{k}\cdot\mathbf{u}_{\beta j})(\mathbf{k}\cdot\mathbf{u}_{\gamma l}) - (\mathbf{k}\cdot\mathbf{u}_{\beta j})(\mathbf{k}\cdot\mathbf{u}_{\beta j})]$$

$$= -\frac{Z_\alpha e^2}{\Omega}\sum_{\beta j}^{N_\beta} Z_\beta \int_{-\infty}^{t} \sum_{\mathbf{k}} \chi_e(\mathbf{k}, t-t')V^{ie}(\mathbf{k})dt' e^{-i\mathbf{k}\cdot(\mathbf{R}_{\gamma l}-\mathbf{R}_{\beta j})}$$

$$\times \left[\mathbf{k}\mathbf{k}\cdot\frac{1}{N_\beta}\sum_{\mathbf{k}'\in\mathbf{K}} e^{i\mathbf{k}'\cdot\mathbf{R}_{\beta j}}\mathbf{q}_{\beta\mathbf{k}'}(t') - \mathbf{k}\mathbf{k}\cdot\frac{1}{N_\alpha}\sum_{\mathbf{k}'\in\mathbf{K}} e^{i\mathbf{k}'\cdot\mathbf{R}_{\alpha i}}\mathbf{q}_{\alpha\mathbf{k}'}(t')\right]$$

$$= -\frac{Z_\alpha e^2}{\Omega}\sum_{\beta j}^{N_\beta} Z_\beta \int_{-\infty}^{t} \sum_{\mathbf{k}} \chi_e(\mathbf{k}, t-t')V^{ie}(\mathbf{k})dt'$$

$$\times \left[\frac{1}{N_\beta}\mathbf{k}\mathbf{k}\cdot\sum_{\mathbf{k}'\in\mathbf{K}} e^{i\mathbf{k}'\cdot\mathbf{R}_{\alpha i}}e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_{\beta l}}\mathbf{q}_{\beta\mathbf{k}'}(t') - \frac{1}{N_\alpha}\mathbf{k}\mathbf{k}\cdot\sum_{\mathbf{k}'\in\mathbf{K}} e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}_{\alpha i}}e^{-i\mathbf{k}'\cdot\mathbf{R}_{\beta l}}\mathbf{q}_{\alpha\mathbf{k}'}(t')\right]$$

$$= -\frac{Z_\alpha e^2}{\Omega}\sum_{\beta}^{N_\beta} Z_\beta \int_{-\infty}^{t} \sum_{m\mathbf{k}} e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}dt'$$

$$\times \left[\chi_e(\mathbf{k}+\mathbf{K}_m, t-t')V^{ie}_{\mathbf{k}+\mathbf{K}_m}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta\mathbf{k}}(t')\right.$$

$$\left.-\frac{N_\beta}{N_\alpha}\chi_e(\mathbf{K}_m, t-t')V^{ie}_{\mathbf{K}_m}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha\mathbf{k}}\right],$$

The Fourier transform of $\chi_e(\mathbf{k},\omega)$ with respect to time:

$$\chi_e(\mathbf{k},t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\chi_e(\mathbf{k},\omega)e^{-i\omega t}d\omega$$

where

$$\chi_e(\mathbf{k},t) = \ 0 \quad \text{if } t<0$$

See Appendix B for details. Then

$$[\mathbf{1}] = -\frac{Z_\alpha e^2}{2\pi\Omega}\sum_\beta^{N_\beta} Z_\beta \sum_{m\mathbf{k}}\int_{-\infty}^{\infty} e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}d\omega\int_{-\infty}^{\infty}e^{-i\omega(t-t')}$$

$$\left[\chi_e(\mathbf{k}+\mathbf{K}_m,\omega)V^{ie}_{\mathbf{k}+\mathbf{K}_m}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta\mathbf{k}}(t')\right.$$

$$\left.-\frac{N_\beta}{N_\alpha}\chi_e(\mathbf{K}_m,\omega)V^{ie}_{\mathbf{K}_m}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha\mathbf{k}}(t')\right]dt'$$

$$= -\frac{Z_\alpha e^2}{2\pi\Omega}\sum_\beta^{N_\beta} Z_\beta\sum_{m\mathbf{k}}\int_{-\infty}^{\infty}e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}}e^{-i\omega t}d\omega$$

$$\left[\chi_e(\mathbf{k}+\mathbf{K}_m,\omega)V^{ie}_{\mathbf{k}+\mathbf{K}_m}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta\mathbf{k}}(\omega)\right.$$

$$\left.-\frac{N_\beta}{N_\alpha}\chi_e(\mathbf{K}_m,\omega)V^{ie}_{\mathbf{K}_m}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha\mathbf{k}}(\omega)\right].$$

The second part of (C.4) is

$$[\mathbf{2}] = -e\nabla_{\alpha j}\sum_{\beta i}^{N_\beta} Z_\beta\int_\Omega\int_{-\infty}^{t}\chi_e(\mathbf{r}-\mathbf{r}', t-t')\rho_{ext}(\mathbf{r}',t')d^3r'dt'V^{ie}(\mathbf{r}-\mathbf{R}_{\beta j})d^3r$$

$$= -\frac{e}{\Omega^3}\nabla_{\alpha j}\sum_{\beta i}^{N_\beta} Z_\beta \int_\Omega \int_{-\infty}^{t} \sum_{\mathbf{k}\mathbf{k}'\mathbf{k}''} V^{ie}(\mathbf{k})\chi_e(\mathbf{k}', t-t')\rho_{ext}(\mathbf{k}'', t')$$

$$e^{-i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R}_{\beta i})} e^{i\mathbf{k}'\cdot(\mathbf{r}-\mathbf{r}')} e^{i\mathbf{k}''\cdot\mathbf{r}'} d^3r' d^3r dt'$$

$$= -\frac{e}{\Omega}\nabla_{\alpha j}\sum_{\beta i}^{N_\beta} Z_\beta \int_\Omega \int_{-\infty}^{t} \sum_{\mathbf{k}} V^{ie}(\mathbf{k})\chi_e(\mathbf{k}, t-t')\rho_{ext}(\mathbf{k}, t') e^{-i\mathbf{k}\cdot\mathbf{R}_{\beta i}} dt'$$

$$= -i\frac{e}{\Omega} Z_\alpha \int_{-\infty}^{\infty} \sum_{\mathbf{k}} \mathbf{k} V^{ie}(\mathbf{k})\chi_e(\mathbf{k}, t-t')\rho_{ext}(\mathbf{k}, t') e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha j}} dt'$$

$$= -i\frac{eZ_\alpha}{2\pi\Omega}\sum_{\mathbf{k}} \mathbf{k} V^{ie}(\mathbf{k}) \int_{-\infty}^{\infty} \chi_e(\mathbf{k}, \omega)\rho_{ext}(\mathbf{k}, \omega) e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha j}} e^{-i\omega t} d\omega.$$

Thus, the form required in Chapter 3 is

$$\nabla_{\alpha i}\sum_{\beta} Z_\beta e^2 \sum_{j}^{N_\beta} \int_\Omega n_e(\mathbf{r}, t) V^{ie}(\mathbf{r} - \mathbf{R}_{\beta j}) d^3r$$

$$= -\frac{Z_\alpha e^2}{\Omega}\sum_{\beta} Z_\beta \sum_{m, \mathbf{k}\in\mathbf{K}} \int_{-\infty}^{\infty} [\chi_e(\mathbf{k}+\mathbf{K}_m, \omega) V^{ie}_{\mathbf{k}+\mathbf{K}_m}(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\cdot\mathbf{q}_{\beta\mathbf{k}}(\omega)$$

$$-\frac{N_\beta}{N_\alpha}\chi_e(\mathbf{K}_m, \omega) V^{ie}_{\mathbf{K}_m}\mathbf{K}_m\mathbf{K}_m\cdot\mathbf{q}_{\alpha\mathbf{k}}(\omega)] e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}} e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}} e^{-i\omega t} d\omega$$

$$-\frac{i4\pi e Z_\alpha}{\Omega}\sum_{\mathbf{k}} \frac{\mathbf{k}}{\mathbf{k}^2} \int_{-\infty}^{\infty} \chi_e(\mathbf{k}, \omega)\rho_{ext}(\mathbf{k}, \omega) e^{i\mathbf{k}\cdot\mathbf{R}_{\alpha i}} e^{-i\omega t} d\omega \qquad \text{(C.5)}$$

APPENDIX D

The Form of $\mathbf{k} \cdot \mathbf{q}_{\alpha \mathbf{k}}$

In a long-wave length limit, i.e., for small$\mathbf{k}$, equation (3.23) can be written as,

$$-\frac{M_\alpha}{N_\alpha}\omega^2 \mathbf{q}_{\alpha k}(\omega) = -\frac{1}{\Omega}\sum_\beta \mathbf{k}\mathbf{k}\cdot\mathbf{q}_{\beta k} W^{\alpha\beta}(\mathbf{k}) - \frac{i4\pi e Z_\alpha \mathbf{k}\rho_{ext}(\mathbf{k},\omega)}{\Omega k^2 \varepsilon_e(\mathbf{k},\omega)}. \tag{D.1}$$

By multiplying a factor $\frac{\Omega}{4\pi Z_\alpha e}\mathbf{k}$ to both side of equation (D.1), we get

$$\frac{\omega^2}{\omega_\alpha^2} Z_\alpha e \mathbf{k}\cdot\mathbf{q}_{\alpha k}(\omega) = \sum_\beta k^2 Z_\beta e \mathbf{k}\cdot\mathbf{q}_{\beta k}\frac{W^{\alpha\beta}(\mathbf{k})}{4\pi Z_\alpha Z_\beta e^2} - \frac{i\rho_{ext}(\mathbf{k},\omega)}{\varepsilon_e(\mathbf{k},\omega)}, \tag{D.2}$$

where $\omega_\alpha^2 = \frac{4\pi(Z_\alpha e)^2 N_\alpha}{M_\alpha \Omega}$.

In the long-wave length limit, the longitudinal ion plasma frequency for each species α (ignoring the interaction with electrons) is of the form $\omega_{I(\alpha)}^2(\mathbf{k}) = \omega_{I(\alpha)}^2 + \beta_{I(\alpha)}^2 k^2$. This gives

$$\frac{k^2 W_{\mathbf{k}}^{\alpha\beta}}{4\pi Z_\alpha Z_\beta e^2} = \begin{cases} \frac{1}{\varepsilon_e(\mathbf{k},\omega)} + \frac{\beta_\alpha^2 k^2}{\omega_\alpha^2} & \text{if } \alpha = \beta \\ \frac{1}{\varepsilon_e(\mathbf{k},\omega)} & \text{otherwise} \end{cases} \tag{D.3}$$

Substituting equation (D.3) into equation (D.2), gives

$$(1+\Omega_\alpha) Z_\alpha e\mathbf{k}\cdot\mathbf{q}_{\alpha k} + \sum_{\beta_{\beta\neq\alpha}} Z_\beta e\mathbf{k}\cdot\mathbf{q}_{\beta k} = -i\rho_{ext}(\mathbf{k},\omega) \tag{D.4}$$

where $\Omega_\alpha = \frac{\beta_\alpha^2 k^2 - \omega^2}{\omega_\alpha^2}\varepsilon_e(\mathbf{k},\omega)$.

For entire species of ions, equation (D.4) can be written in a matrix form

$$\mathbf{AB} = \mathbf{C} \tag{D.5}$$

where

$$\mathbf{A}=\begin{pmatrix} 1+\Omega_1 & 1 & 1 & \cdots & 1 \\ 1 & 1+\Omega_2 & 1 & \cdots & 1 \\ 1 & 1 & 1+\Omega_3 & \cdots & 1 \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 1 & \cdot & \cdot & \cdots & 1+\Omega_n \end{pmatrix},$$

$$\mathbf{B}=\begin{pmatrix} Z_1 e\mathbf{k}\cdot\mathbf{q}_{1k} \\ Z_2 e\mathbf{k}\cdot\mathbf{q}_{2k} \\ Z_3 e\mathbf{k}\cdot\mathbf{q}_{3k} \\ \cdot \\ \cdot \\ \cdot \\ Z_n e\mathbf{k}\cdot\mathbf{q}_{nk} \end{pmatrix}$$

and

$$\mathbf{C}=-i\rho_{ext}(\mathbf{k},\omega)\begin{pmatrix} 1 \\ 1 \\ 1 \\ \cdot \\ \cdot \\ \cdot \\ 1 \end{pmatrix}.$$

Then matrix $\mathbf{B}$ can be obtained as

$$\mathbf{B}=\mathbf{A}^{-1}\mathbf{C}. \tag{D.6}$$

Skipping all the algebra, the inverse of matrix $\mathbf{A}$ can be written as

$$\mathbf{A}^{-1}=\begin{pmatrix} \frac{1}{\Omega_1}-\frac{1}{\Omega_1^2(1+\sum_n\frac{1}{\Omega_n})} & \frac{-1}{\Omega_1\Omega_2(1+\sum_n\frac{1}{\Omega_n})} & \cdots & \frac{-1}{\Omega_1\Omega_n(1+\sum_n\frac{1}{\Omega_n})} \\ \frac{-1}{\Omega_1\Omega_2(1+\sum_n\frac{1}{\Omega_n})} & \frac{1}{\Omega_2}-\frac{1}{\Omega_2^2(1+\sum_n\frac{1}{\Omega_n})} & \cdots & \frac{-1}{\Omega_2\Omega_n(1+\sum_n\frac{1}{\Omega_n})} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \frac{-1}{\Omega_1\Omega_n(1+\sum_n\frac{1}{\Omega_n})} & \cdot & \cdots & \frac{1}{\Omega_n}-\frac{1}{\Omega_n^2(1+\sum_n\frac{1}{\Omega_n})} \end{pmatrix}. \tag{D.7}$$

Finally, a form of $\mathbf{k}\cdot\mathbf{q}_{\alpha\mathbf{k}}$ is obtained which leads to,

$$\begin{aligned} Z_\alpha e \mathbf{k} \cdot \mathbf{q}_{\alpha\mathbf{k}} &= -\frac{1}{\Omega_\beta}\left(1 - \sum_\beta \frac{1}{\Omega_\beta(1+\frac{1}{\Omega_\beta})}\right) i\rho_{ext}(\mathbf{k}_o, \omega_o) \\ &= -\frac{i\rho_{ext}(\mathbf{k}_o, \omega_o)}{\Omega_\alpha(1+\sum_\beta \frac{1}{\Omega_\beta})}. \end{aligned} \tag{D.8}$$

APPENDIX E

Matrix elements for the equation of motion of binary alloy systems

For tackling the difficulty of speeding up the summations in the elements of the dynamic vibration matrix $\Phi(\mathbf{k})$, Ewald-Fuchs method is introduced to achieve the purpose [see Ewald (1921), Ewald (1938) and Kittel (1953)].

The total potential energy W which excludes the external test charge is

$$W = W_a + W_b + W_{vd} + W_{ie}, \tag{E.1}$$

where $W_a + W_b$ is the pure Coulomb potential. W_{vd} stands for the contribution from van der Waals interaction to the total energy of the ionic system. And W_{ie} represents the contribution from electron-ion interaction.

In the ionic system, the real interaction between two ions is

$$V(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) = V_a(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) + V_b(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) + V_{vd}(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) \tag{E.2}$$

V_{vd} is the contribution from the non-Coulombic interaction. The dominant non Coulombic interaction would be of the van der Waals type, and is considered here.

Then the real potential energy of the system can be written as

$$\frac{1}{2}\sum_{\alpha,\beta}\sum_{i,j} V(\mathbf{R}_{\alpha i} - \mathbf{R}_{\beta j}) = W_a + W_b + W_{vd} \tag{E.3}$$

Let W_a, which is a part of Coulomb potential energy, be

$$W_a = \frac{4\pi q^2}{2\Omega}\sum_{\mathbf{k}}\sum_{\alpha,\beta}\sum_{i,j}\frac{exp(-i\mathbf{k}\cdot\mathbf{R}^{ij}_{\alpha\beta})exp(-k^2/4\eta)}{k^2}$$

$$\times \left[1 + (\mathbf{k}\cdot\mathbf{u}_\alpha^l)(\mathbf{k}\cdot\mathbf{u}_\beta^l) - \frac{1}{2}[(\mathbf{k}\cdot\mathbf{u}_\alpha^l)^2 + (\mathbf{k}\cdot\mathbf{u}_\beta^l)^2]\right], \tag{E.4}$$

where the distance between any two ions is

$$\mathbf{R}_{\alpha\beta}^{ij} = \mathbf{R}_\alpha^l - \mathbf{R}_\beta^j.$$

Let W_b, which is the rest of total Coulomb potential energy, be

$$W_b = \frac{1}{2}q^2 \sum_{\alpha\beta}\sum_{l,j}\left\{\frac{1 - G(\eta^{\frac{1}{2}}|\mathbf{R}_{\alpha\beta}^{lj}|)}{|\mathbf{R}_{\alpha\beta}^{lj}|^3}\left[-\frac{(\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)^2}{2} + \frac{3}{2|\mathbf{R}_{\alpha\beta}^{lj}|^2}[\mathbf{R}_{\alpha\beta}^{lj}\cdot(\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)]^2\right]\right.$$

$$\left. + 2\sqrt{\frac{\eta}{\pi}}\frac{exp(-\eta(\mathbf{R}_{\alpha\beta}^{lj})^2)}{|\mathbf{R}_{\alpha\beta}^{lj}|^2}\left[-\frac{(\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)^2}{2} + (\frac{3}{2|\mathbf{R}_{\alpha\beta}^{lj}|^2} + \eta)[\mathbf{R}_{\alpha\beta}^{lj}\cdot(\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)]^2\right]\right\} \tag{E.5}$$

where $G(x)$ is the error function,

$$G(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-z^2)dz. \tag{E.6}$$

Equation (E.4) and (E.5) are formulas which are derived by introducing two Gaussian distributions of charge of opposite sign centred at each lattice point [see Ewald (1921), Ewald (1938), Kittel (1953) and Clark (1958)] The sum over l is the potential due to the point charges, each surrounded by a Gaussian distribution of charge of the opposite sign. The parameter η is the square of the half-width of each of the Gaussian distributions which can be adjusted to achieve rapid convergence in the calculation.

W_{vd}, which is energy from van der Waals interaction, is

$$W_{vd} = \frac{1}{2}\sum_{\alpha\beta}\sum_{lj}[V_{vd}(\mathbf{R}_{\alpha\beta}^{lj}) + (\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)\cdot\nabla_{\alpha l}\nabla_{\alpha j}V_{vd}(\mathbf{R}_{\alpha\beta}^{lj})\cdot(\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)]. \tag{E.7}$$

The term of the first order in $(\mathbf{u}_\alpha^l - \mathbf{u}_\beta^j)$ vanishes because of the symmetric structure in the system.

E.1 Calculation of the potential W_a

The force on the i-th ion of γ species will depend in part on $-\nabla_{\gamma i} W_a$. This derivative is found from equation (E.4) to be

$$-\nabla_{\gamma i} W_a =$$

$$\frac{-4\pi q^2 N_\alpha}{\Omega} \sum_{m\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}^i_\gamma} \Big\{ [F(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m) - F(\mathbf{K}_m)\mathbf{K}_m\mathbf{K}_m] \cdot \mathbf{q}_{\gamma\mathbf{k}}$$

$$+ \left[F(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m) \cdot \mathbf{q}_{\beta\mathbf{k}} - F(\mathbf{K}_m)\mathbf{K}_m\mathbf{K}_m \cdot \mathbf{q}_{\gamma\mathbf{k}} \right] e^{i\mathbf{K}_m\cdot\mathbf{R}_{\gamma\beta}} \Big\}. \quad \text{(E.8)}$$

In a binary system, there are two species ions. Let them be α and β. The kth term of the summation in the above expression for the two species is $-(\nabla_{\alpha i} + \nabla_{\beta i})W_a$, and its form in reciprocal space is

$$-\frac{1}{M_\alpha \omega_\alpha^2} [(\nabla_{\alpha i} + \nabla_{\beta i})W_a]_{\mathbf{k}} =$$

$$\frac{-4\pi q^2 N_\alpha}{\Omega M_\alpha \omega_\alpha^2} \sum_m \{ [F(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m) - F(\mathbf{K}_m)\mathbf{K}_m\mathbf{K}_m] \cdot$$

$$+ [F(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m) - F(\mathbf{K}_m)\mathbf{K}_m\mathbf{K}_m] \cdot e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}} \Big\} (\mathbf{q}_{\alpha\mathbf{k}} + \mathbf{q}_{\beta\mathbf{k}}), \quad \text{(E.9)}$$

where

$$F(\mathbf{k}) = \frac{exp(-\frac{|\mathbf{k}|^2}{4\eta})}{|\mathbf{k}|^2}. \quad \text{(E.10)}$$

E.2 Calculation of the potential W_b

The force on the i-th ion of γ species will also depend in part on $-\nabla_{\gamma i} W_b$. This derivative is found from equation (E.5) to be

$$-\nabla_{\gamma i} W_b = -q^2 \sum_{j\beta} \left\{ G^{ij}_{\alpha\beta}[-(\mathbf{u}^i_\gamma - \mathbf{u}^j_\beta) + \frac{3}{(\mathbf{R}^{ij}_{\gamma\beta})^2} \mathbf{R}^{ij}_{\gamma\beta} \cdot (\mathbf{u}^i_\gamma - \mathbf{u}^j_\beta)\mathbf{R}^{ij}_{\gamma\beta}] \right.$$

$$+H^{lj}_{\alpha\beta}[-(\mathbf{u}^i_\gamma - \mathbf{u}^j_\beta) + (\frac{3}{(\mathbf{R}^{ij}_{\gamma\beta})^2} + 2\eta)\mathbf{R}^{ij}_{\gamma\beta} \cdot (\mathbf{u}^i_\gamma - \mathbf{u}^j_\beta)\mathbf{R}^{ij}_{\gamma\beta}]\Big\}, \tag{E.11}$$

where

$$G^{lj}_{\alpha\beta} = \frac{1 - G(\eta^{\frac{1}{2}}|\mathbf{R}^{lj}_{\alpha\beta}|)}{|\mathbf{R}^{lj}_{\alpha\beta}|^3} \tag{E.12}$$

and

$$H^{lj}_{\alpha\beta} = 2\sqrt{\frac{\eta}{\pi}}\frac{exp(-\eta(\mathbf{R}^{lj}_{\alpha\beta})^2)}{|\mathbf{R}^{lj}_{\alpha\beta}|^2}. \tag{E.13}$$

The k-th term of the force on the γ species ion is $-\nabla_{\gamma i}W_b$ in reciprocal space, and is

$$\begin{aligned}-\frac{1}{M_\gamma\omega^2_\gamma}[\nabla_{\gamma i}W_b]_{\mathbf{k}} = \frac{q^2}{M_\gamma\omega^2_\alpha}\sum_{j\beta}\Big\{&G^{lj}_{\gamma\beta}[(\mathbf{q}_{\gamma\mathbf{k}} - \mathbf{q}_{\beta\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\gamma i})})\\ &-\frac{3}{(\mathbf{R}^{ij}_{\gamma\beta})^2}\mathbf{R}^{ij}_{\gamma\beta} \cdot (\mathbf{q}_{\gamma\mathbf{k}} - \mathbf{q}_{\beta\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\gamma i})})\mathbf{R}^{ij}_{\gamma\beta}]\\ &+H^{lj}_{\gamma\beta}[(\mathbf{q}_{\gamma\mathbf{k}} - \mathbf{q}_{\beta\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\gamma i})})\\ &-(\frac{3}{(\mathbf{R}^{ij}_{\gamma\beta})^2} + 2\eta)\mathbf{R}^{ij}_{\gamma\beta} \cdot (\mathbf{q}_{\gamma\mathbf{k}} - \mathbf{q}_{\beta\mathbf{k}}e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\gamma i})})\mathbf{R}^{ij}_{\gamma\beta}]\Big\}.\end{aligned} \tag{E.14}$$

For the binary system with only two species, the k-th term of the summation in the force from the two species is $-(\nabla_{\alpha i} + \nabla_{\beta i})W_b$, and its form in reciprocal space is,

$$\begin{aligned}-\frac{1}{M_\alpha\omega^2_\alpha}[(\nabla_{\alpha i} + \nabla_{\beta i})W_b]_{\mathbf{k}} = \frac{q^2}{M_\alpha\omega^2_\alpha}\sum_j(\mathbf{q}_{\alpha\mathbf{k}} + \mathbf{q}_{\beta\mathbf{k}})\Big\{&(e^{i\mathbf{k}\cdot(\mathbf{R}_{\alpha j}-\mathbf{R}_{\alpha i})} - 1)\\ &\times\Big[G^{lj}_{\alpha\alpha}(\frac{3}{(\mathbf{R}^{ij}_{\alpha\alpha})^2}\mathbf{R}^{ij}_{\alpha\alpha}\mathbf{R}^{ij}_{\alpha\alpha} - \mathbf{I}) + H^{lj}_{\alpha\alpha}[(\frac{3}{(\mathbf{R}^{ij}_{\alpha\alpha})^2} + 2\eta)\mathbf{R}^{ij}_{\alpha\alpha}\mathbf{R}^{ij}_{\alpha\alpha} - \mathbf{I}]\Big]\\ &+(e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\alpha i})} - 1)\\ &\times\Big[G^{lj}_{\alpha\beta}(\frac{3}{(\mathbf{R}^{ij}_{\alpha\beta})^2}\mathbf{R}^{ij}_{\alpha\beta}\mathbf{R}^{ij}_{\alpha\beta} - \mathbf{I}) + H^{lj}_{\alpha\beta}[(\frac{3}{(\mathbf{R}^{ij}_{\alpha\beta})^2} + 2\eta)\mathbf{R}^{ij}_{\alpha\beta}\mathbf{R}^{ij}_{\alpha\beta} - \mathbf{I}]\Big]\Big\}.\end{aligned} \tag{E.15}$$

E.3 The contribution from van der Waals interaction W_{vd}

Finally, the force on the i-th ion of γ species will also depend in part on the non-Coulomb potential, and is $-\nabla_{\gamma i} W_{vd}$. This derivative is found from equation (E.7) to be

$$-[\nabla_{\gamma i} W_{vd}]_{\mathbf{k}} =$$

$$\sum_{j\beta} \left[e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\alpha i})} \nabla_{\gamma i}\nabla_{\gamma j} V_{vd}(\mathbf{R}_{\beta j}-\mathbf{R}_{\alpha i})\cdot \mathbf{q}_{\beta\mathbf{k}} - \nabla_{\gamma i}\nabla_{\gamma j} V_{vd}(\mathbf{R}_{\beta j}-\mathbf{R}_{\alpha i})\cdot \mathbf{q}_{\alpha\mathbf{k}} \right] \tag{E.16}$$

As before, in the binary system the **k**-th term of the summation in the force from the non-Coulombic potential on the two species in a reciprocal space has the form,

$$-\frac{1}{M_\alpha \omega_\alpha^2}[(\nabla_{\alpha i}+\nabla_{\beta i})W_{vd}]_{\mathbf{k}} = \frac{1}{M_\alpha \omega_\alpha^2}\sum_j \left[(e^{i\mathbf{k}\cdot(\mathbf{R}_{\alpha j}-\mathbf{R}_{\alpha i})}-1)\nabla_{\alpha i}\nabla_{\alpha j} V_{vd}(\mathbf{R}_{\alpha j}-\mathbf{R}_{\alpha i}) \right.$$

$$\left. +(e^{i\mathbf{k}\cdot(\mathbf{R}_{\beta j}-\mathbf{R}_{\alpha i})}-1)\nabla_{\alpha i}\nabla_{\alpha j} V_{vd}(\mathbf{R}_{\beta j}-\mathbf{R}_{\alpha i}) \right]\cdot(\mathbf{q}_{\alpha\mathbf{k}}+\mathbf{q}_{\beta\mathbf{k}}) \tag{E.17}$$

E.4 Contribution to the dynamic matrix from electron-ion interaction

As mentioned in the first part of this appendix, W_{ie} is a total potential energy from the contribution of electron-ion interaction in the system. In a binary system which include two ion species only and from equations (3.23) and (3.24), the kth term of the summation of the force on the two species from electron-ion interaction $-(\nabla_{\alpha i}+\nabla_{\beta i})W_a$ in reciprocal space can be immediately worked out as

$$-\frac{1}{M_\alpha \omega_\alpha^2}[(\nabla_{\alpha i}+\nabla_{\beta i})W_{ie}]_{\mathbf{k}} =$$

$$\sum_m [(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\Psi(\mathbf{k}+\mathbf{K}_m) - \mathbf{K}_m\mathbf{K}_m\Psi(\mathbf{K}_m)]\,(1+e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}). \tag{E.18}$$

E.5 Dynamic matrix of binary alloy system

Using the above results and using an ion plasma frequency

$$\omega_\alpha^2 = \frac{4\pi q^2 N_\alpha}{\Omega M_\alpha}, \tag{E.19}$$

the dynamic matrix for a binary alloy system can be written as

$$\begin{aligned}\Phi(\mathbf{k}) &= \sum_m [(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)F_c(\mathbf{k}+\mathbf{K}_m) - \mathbf{K}_m\mathbf{K}_m F_c(\mathbf{K}_m)]\,(1+e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}}) \\ &\quad -\frac{\Omega}{4\pi N_\alpha}\sum_j \left[\mathbf{T}^{ij}_{\alpha\alpha}+\mathbf{T}^{ij}_{\alpha\beta}\right] \\ &\quad +\frac{\Omega}{4\pi(Z_\alpha e)^2 N_\alpha}\sum_j \left[\mathbf{Y}^{ij}_{\alpha\alpha}+\mathbf{Y}^{ij}_{\alpha\beta}\right] \\ &\quad +\sum_m [(\mathbf{k}+\mathbf{K}_m)(\mathbf{k}+\mathbf{K}_m)\Psi(\mathbf{k}+\mathbf{K}_m) - \mathbf{K}_m\mathbf{K}_m\Psi(\mathbf{K}_m)]\,(1+e^{i\mathbf{K}_m\cdot\mathbf{R}_{\alpha\beta}})\end{aligned} \tag{E.20}$$

where

$$F_c(\mathbf{k}) = \frac{\exp(-|\mathbf{k}|^2/4\eta)}{|\mathbf{k}|^2}, \tag{E.21}$$

$$\mathbf{Y}^{ij}_{\alpha\beta} = (e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\alpha\beta}}-1)\nabla_{\alpha i}\nabla_{\beta i}V_{vd}(\mathbf{R}^{ij}_{\alpha\beta}), \tag{E.22}$$

$$V_{vd}(r) = -\frac{3\hbar}{r^6\pi}\int_0^\infty \frac{d\xi\cdot\xi^4\alpha_\alpha(i\xi)\alpha_\beta(i\xi)}{(\omega_e^2+\xi^2)^2}, \tag{E.23}$$

$$\alpha_i(i\xi) = \frac{e^2 n_i}{m(\omega_i^2+\xi^2)}, \tag{E.24}$$

$$\begin{aligned}\mathbf{T}^{ij}_{\alpha\beta} &= (e^{i\mathbf{k}\cdot\mathbf{R}^{ij}_{\beta\alpha}}-1) \\ &\times \left[G^{ij}_{\beta\alpha}\left(\frac{3}{(R^{ij}_{\beta\alpha})^2}\mathbf{R}^{ij}_{\beta\alpha}\mathbf{R}^{ij}_{\beta\alpha}-\mathbf{I}\right)+H^{ij}_{\beta\alpha}\left(2\left(\frac{3}{2(R^{ij}_{\beta\alpha})^2}+\eta\right)\mathbf{R}^{ij}_{\beta\alpha}\mathbf{R}^{ij}_{\beta\alpha}-\mathbf{I}\right)\right],\end{aligned} \tag{E.25}$$

$$\Psi(\mathbf{k}) = \left(\frac{1}{\varepsilon_e(\mathbf{k})}-1\right)V^{ie}(\mathbf{k}). \tag{E.26}$$

$\alpha_\beta(i\xi)$ is electric dipole polarisabilities of ion species β (at the imaginary frequency $i\xi$).

For derivation of equations (E.23) which is the van der Waals interaction, and (E.24) which is a formula for calculating the electric dipole polarisability of the ion species β, see Mahanty and Taylor (1978).

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