MANY BODY EFFECTS IN HOMOGENEOUS AND INHOMOGENEOUS ELECTRON SYSTEMS

CHAYANIKA SHAH

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY, BOMBAY
1983

MANY BODY EFFECTS IN HOMOGENEOUS AND INHOMOGENEOUS ELECTRON SYSTEMS

THESIS

Submitted in partial fulfilment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

by

CHAYANIKA SHAH

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY,
BOMBAY

1985

THESIS APPROVAL SHEET

Thesis entitled 'MANY BODY EFFECTS IN HOMOGENEOUS AND INHOMOGENEOUS ELECTRON SYSTEMS' by Chayanika Shah is approved for the degree of DOCTOR OF PHILOSOPHY.

Examiners

C. K. Majumdar

Supervisor(s)

Chairman

Date: 7.2.1986

" I could have done it in a much more complicated way" said the red Queen...
-LEWIS CARROLL.

CONTENTS

CHAPTER			Page
1		INTRODUCTION	1
2		GENERAL FORMULATION AND REVIEW..	10
	2.1	Response formalism and definitions	11
	2.2	Exact sum rules	22
	2.2.1	Positivity of g(r) ..	22
	2.2.2	Moment sum rules ..	22
	2.2.3	Compressibility sum rule ..	23
	2.2.4	Dispersion and damping of plasmons	25
	2.3	Review of earlier theories ..	25
	2.4	Description and objectives of the present approach ..	38
3		PRESENT THEORY FOR A COMPLEX FREQUENCY DEPENDENT LOCAL FIELD CORRECTION	41
	3.1	Theoretical formulation of the theory	42
	3.2	Time depend local field - first approximation	47
	3.3	Numerical calculations and results	53
	3.3.1	Damping coefficient of long wave-length plasmons	55
	3.3.2	Finite q and ω calculations ..	59
	3.4	A critique of the approximation.	70

Contd.....

CONTENTS (Contd.)

CHAPTER			Page
4		AN IMPROVED APPROXIMATION FOR $G(q,\omega)$	72
	4.1	Determination of $\bar{D}^{(2)}$ via linear response theory.. ..	73
	4.2	Contributions to $ImG_1(q,\omega)$ in small q limit	83
	4.3	Extraction of $\bar{C}^{(2)}$ from the equation of motion for $f^{(2)}$ ..	89
	4.4	Expression for $\bar{D}^{(2)}$ using response theory	96
	4.5	Evaluation of $f^{(2)eq}_{k\sigma k'\sigma'}(q,q',\omega)$ ..	109
	4.6	Discussion	115
5		DYNAMIC IMAGE POTENTIAL ..	120
	5.1	Review	121
	5.2	Theoretical formulation ..	123
	5.2.1	Model Hamiltonian approach ..	124
	5.2.2	Microscopic dielectric response approach	132
	5.3	Results	138
	5.4	Discussion	153
6		DYNAMIC INTERACTION BETWEEN ATOM OR MOLECULE AND A METALLIC SURFACE.	158
	6.1	Dynamic van der Waals interaction between an atom or molecule and a metallic surface.	159
	6.1.1	Model Hamiltonian approach ..	160
	6.1.2	Response function approach ..	162

Contd.....

CONTENTS (Contd.)

CHAPTER			Page
6			
	6.2	Atom approaching a metal surface with a layer of adsorbed molecules ..	167
	6.3	Disucssion	172
		APPENDIX I	173
		APPENDIX II	180
		APPENDIX III	182
		APPENDIX IV	184
		APPENDIX V	186
		APPENDIX VI	190
		REFERENCES	194
		ACKNOWLEDGEMENTS ..	200
		SUMMARY	

CHAPTER 1

INTRODUCTION

In the study of the macroscopic properties of a system, broadly, two aspects are of interest. One, the response of a system to an external perturbation, when the external perturbation (e.g., in the form of an electric field or magnetic field) acts on the system, and the other the explicit interaction between the external perturbation and the system itself. In this thesis which has been divided into two parts, we study the microscopic many body effects in these two aspects, especially for many electron systems.

The first part deals with the response of an homogeneous electron system, representative of an infinite perfect conductor (metal), to a weak external perturbing scalar potential. In general, in a real metal the interactions of the electrons, which can be approximated as a degenerate fluid, are very complicated because the electrons interact with the positive ionic lattices as well as with other electrons. The difficulty of handling the effect of the lattice is often circumvented, at least for simple metals (e.g., Na, K etc.) by ignoring the lattice ion interaction as a first approximation and then incorporating the lattice ion effect via perturbation theory (e.g., using pseudo potentials). Thus a well accepted model

for simple metals is the so called jellium wherein the positive ions are considered stationary and uniformly smeared out so that the electrons move freely in a constant potential due to the rigid uniform positive background. Within this model, we study the many body effects in the homogeneous electron system. In the second part we study the interaction of a semi-infinite jellium, which now is a representative of a simple metal with a planar surface, with an external perturbation due to an external charge or atom (or molecule).

When a perturbing scalar potential ϕ_{ext}, due to a charge density $n_{ext}(\underset{\sim}{r}, t)$ that couples with the density fluctuations of a system, acts on a homogeneous electron system, the response of the system is described by the retarded density-density response function $\chi^r(\underset{\sim}{r}, t)$[1]. This response function is related to the dielectric function which then contains information about the static and dynamic correlations in the system. In particular, the spatial and temporal Fourier transform of the response function is directly related to experimentally measurable quantities such as electron or X-ray inelastic energy loss spectra. Developing a theory for a space and time dependent dielectric function, which is amenable to computation has therefore been a challenging task for a long time now. The numerical aspect has always set constraints on the nature of the approximations, thus limiting most of the work to approximations accurate only in the long wavelength or high frequency limits. For example, the time

dependent Hartree mean field approximation (also known as random phase approximation, abbreviated RPA) takes proper account of only the long range Coulomb interaction but does not describe correctly the short range exchange and correlation effects.

Several attempts[2,3] have been made to go beyond the RPA. Most of these later theories try to take into account the fact that due to the short range exchange and correlation effects, there is a local depletion in charge density around each electron ; in other words, to each electron is now associated an exchange-correlation hole. This leads to a modification in the time dependent Hartree mean field and one refers to the difference between this new effective field and the mean Hartree field via the so-called local field correction. This local field has been approximated as a static quantity in many of the theories. The static local field approximation implies that an electron moves with its hole held rigidly around it. This is valid only if the perturbing force does not vary rapidly with time, so that the hole finds time to adjust itself along with the external force. In the case where the external force is rapidly varying with time, the motion of the hole is very complex. It distorts and also performs dynamic motion with respect to the electron. It is essential to have a frequency dependent local field correction to take these effects into account.

Inclusion of dynamic and dissipative effects i.e. a frequency dependent local field correction is also essential to

observe the damping of long wavelength plamons. The X-ray and the electron scattering experiments[4] have shown a double peak structure for the inelastic energy loss spectra at large momentum transfers ($q \simeq 2q_F$, q_F is the Fermi momentum). Because of the diverse nature of the target systems, which exhibit this behaviour, the origin of this double peak structure is considered to be in the exchange and correlation effects rather than in the band structure effects.

In view of the above mentioned aspects, we develop in the first part of the thesis, a theory for the time-dependent local field correction. Working in the equation of motion approach, we solve the equation of motion for the so-called one particle Wigner distribution function, $f^{(1)}$, in the presence of an external field, by decoupling the two particle distribution function $f^{(2)}$ via a scheme often used for classical liquids[5] i.e.,

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t) \cong f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}',t) - \frac{1}{n^2}\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t).$$

Instead of self-consistently solving the equation thus obtained we use different approximations for $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t) = \sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t)$, (a quantity which depends on the external field), and obtain an expression for the local field correction $G(q,\omega)$.

The first approximation that we have studied is based on an ad-hoc approximation suggested by Singwi et al.[6] for the

vertex function appearing in the integral equation for the time ordered correlation function. The numerical calculations that we have carried out are mainly for the dynamic effects in the local field correction. Thus we have calculated the damping coefficient of long wavelength plasons for r_s = 2,3,4 and 5. We have also evaluated the real and imaginary parts of the local field correction for finite momentum transfers and frequencies. For a particular value of the momentum transfer, for which the double peak structure is observed experimentally, we have obtained the dynamic structure factor.

We have further improved upon the ad-hoc approximation for the vertex function by using the linear response theory. In this case also we get a frequency dependent local field correction, from which we have evaluated the damping coefficient of plasmons in the small q limit for r_s in the metallic density range. In the earlier case as well as in this improved approach, we have calculated the damping coefficient in the weak coupling ($r_s \to 0$) limit and compared with the corresponding available perturbative calculation results[7]. In the latter case, a detailed study of $S(\underset{\sim}{q},\omega)$ requires heavy numerical work beyond the available computing facility, and therefore we restrict ourselves here in trying to understand the contents of this approximation. For this purpose we follow two more independent approaches to obtain $C^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$. In one method the function $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ is extracted using an approximate form of the equation of motion

for the two particle distribution function[8]. In the second method, we introduce a response function corresponding to the density-density correlation function $D^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$ (which is related to $C^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$) in the presence of the external field and use its equation of motion to obtain $D^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$. The improved approximation for $G(\underset{\sim}{q}, \omega)$ then follows as a special case from these two alternative approaches.

Finally, we also obtain an expression for $f^{(2)eq}$, the two particle distribution function in equilibrium i.e., in the absence of an external field, using the equation of motion approach. This quantity appears in the improved approximation for $G(\underset{\sim}{q}, \omega)$, as well as in the approximations developed by other workers[8-10]. However, the latter workers[10], used ansätze for $f^{(2)eq}$ rather than trying to evaluate it. To our knowledge, our expression for $f^{(2)eq}$ which is compatible with RPA is the first theoretical formula given.

In the second part of the thesis we study the interaction of a semi-infinite jellium with an incoming charged particle or a dipole. To circumvent the difficulties arising from the inhomogeneity , we work mainly within the model Hamiltonian approach. The scattering experiments such as low energy electron diffraction and fast electron spectroscopy[4], studying surface phenomena require a better knowledge of the dynamic image potential which is the interaction between a moving charged particle and the surface excitations at the metal. Most of the

earlier studies have assumed that the charged particle moves at a constant speed[11]. We have carried out calculations here taking the acceleration of the particle also into account[12]. We also show, for the first time, how a local speed approximation in a self-consistent scheme[13] is justified. Similarly atom beam scattering[14] and adsorption experiments[15] have renewed interest in the van der Waals interaction which forms the attractive part of the interaction between an atom and a metal surface. The large discrepancy between experiment and theory for the strength of this interaction has initiated a lot of theoretical work[16] in this field. We study the effect of the velocity of the approaching atom on this interaction. In view of the fact that already adsorbed atoms can affect the van der Waals interaction we have also studied within a pure image model, the single loss probability for an atom or molecule approaching a metal surface with an uniform layer of adsorbed molecules. The derived formulae, to our knowledge are new.

The chapterwise breakup of this thesis is as follows.

We begin Chapter 2 with same requisite basic definitions for an electron gas system and a description of the exact sum rules that any homogeneous electron system is expected to satisfy. We then give a brief review of the various available theories for the space and time-dependent dielectric function. We end this chapter with a brief outline of the approach developed in this thesis.

In Chapter 3 we give the basic approximation of the theory and then discuss in detail the first approximation for $C^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$. This chapter also contains the results for the numerical calculations for the damping coefficient of long wavelength plasmons ; for the local field correction at finite q and ω and for $S(\underset{\sim}{q}, \omega)$. A critique of this approximation is given at the end.

Chapter 4 describes in detail the linear response theory approximation for $C^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$ and also gives the results for damping obtained in this case. This chapter also contains a description of the two other approaches followed to obtain $C^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t)$. The conclusions based on this study are given at the end of this chapter.

The second part of this thesis is dealt with in Chapters 5 and 6. Chapter 5 includes the theoretical formulation using two approaches (viz., model Hamiltonian and dielectric response approach) as well as the numerical calculations for the dynamic image potential taking acceleration of the particle into account.

Chapter 6 deals with the dynamic interaction between an atom or molecule with a metallic surface. Here, again using the model Hamiltonian and dielectric response approach we obtain the dynamic van der Waals interaction between an atom or molecule and the metallic surface assuming a constant speed of

the incoming particle. Also given in this chapter are the details for the interaction of an atom or molecule and adsorbed molecules.

CHAPTER 2

GENERAL FORMULATION AND REVIEW

Developing a theory for the space and time dependent dielectric function for a homogeneous electron system (infinite jellium) is a challenging task in the study of many body effects. The dielectric function offers a simple and convenient way to describe many of the properties of the many electron system, e.g., the density fluctuation spectrum $S(q, \omega)$, the dispersion and damping of plasmons etc. Hence a proper, realistic description of this function is important. We make here an attempt in this direction.

We begin this chapter by giving a few basic results for response theory as applied to the homogeneous electron gas (i.e., infinite jellium) system and also defining some relevant quantities. Section (2.2) gives the exact sum rules, i.e., the limiting behaviour of the response function at long wavelength and large frequency. A number of attempts using different approaches have been made to develop a theory that is amenable to numerical computations ; a brief review of these efforts is given in Section (2.3). We conclude this chapter by describing briefly in Section (2.4), the objectives of the present work and the approach followed.

2.1 RESPONSE FORMALISM AND DEFINITIONS

We are interested in studying the response of the system to a weak, time-dependent external perturbation. Since the perturbation is weak, the response is in general, linearly proportional to the external perturbing potential. The perturbation H_1 can then be written as (for brevity, any possible space dependence suppressed),

$$H_1 = - F(t) . A \quad , \qquad (2.1.1)$$

where A is a constant operator and F(t) a function of time representing an external force that vanishes in the infinite past. As a result of the perturbation the average value of any operator B becomes time dependent and its mean value at time t is denoted by $\langle B(t) \rangle$. The linear relation between this quantity and the external potential can be written as [1,17,18]

$$\langle B(t) \rangle - \langle B \rangle = \int_{-\infty}^{t} dt' \, \chi_{BA}(t-t') \, F(t') . \qquad (2.1.2)$$

Here, $\chi_{BA}(t)$, a bounded function of t describes the linear response of the system. The upper bound on the above integral arises due to the causality requirements which make $\chi_{BA}(t)$ vanish for $t < 0$; $\chi_{BA}(t)$ is hence called the retarded response function. A formal expression for the response function is given by,

$$\chi_{BA}(t-t') = (i\hbar)^{-1} \langle [B(t), A(t')]_- \rangle \, \theta(t-t') ,$$

$$= \theta(t-t') \langle [B(t-t'), A(0)]_- \rangle / i\hbar . \qquad (2.1.3)$$

Here, $\theta(t)$ is the Heaviside step function which is defined as follows :

$$\Theta(t) = 1 \quad , \qquad t > 0 \quad ,$$
$$= 0 \quad , \qquad t < 0 \quad . \tag{2.1.4}$$

As a special case, we consider the response of an electron gas system to an external potential $\phi_{ext}(\underset{\sim}{r}, t)$ due to a probe of density $n_e(\underset{\sim}{r}, t)$ which is coupled to the density fluctuations of the system. Then the retarded density-density response function in this case, is given by[19],

$$\chi^r(\underset{\sim}{r}, t ; \underset{\sim}{r}', t') = (i\hbar)^{-1} \Theta(t-t') \langle [\hat{\rho}(\underset{\sim}{r}, t) , \hat{\rho}(\underset{\sim}{r}', t')]_- \rangle ,$$

where $\rho(\underset{\sim}{r},t)$ is the particle density operator. The system that we are considering, i.e., a homogeneous infinite jellium, is translationally invariant and so we can write,

$$\chi^r(\underset{\sim}{r}-\underset{\sim}{r}', t-t') = (i\hbar)^{-1} \Theta(t-t') \langle [\hat{\rho}(\underset{\sim}{r}-\underset{\sim}{r}', t-t') , \hat{\rho}(0,0)]_- \rangle . \tag{2.1.5}$$

The space and temporal Fourier transform $F(\underset{\sim}{q},\omega)$ of any function $F(\underset{\sim}{r},t)$ is defined via ,

$$F(\underset{\sim}{r}, t) = \frac{1}{V} \sum_{\underset{\sim}{q}} \int \frac{d\omega}{2\pi} \, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r} - i\omega t} \, F(q, \omega) . \tag{2.1.6}$$

In this Fourier space, equation (2.1.2) for the present case can then be written as,

$$\bar{n}(\underset{\sim}{q}, \omega) = \chi^r(\underset{\sim}{q}, \omega) \, \phi_{ext}(\underset{\sim}{q}, \omega) , \tag{2.1.7}$$

where, $\bar{n}(\underset{\sim}{q},\omega)$ is the induced density of the system. The external potential due to the charge density $n_e(\underset{\sim}{q},t)$ is given (in Fourier space) by,

$$\phi_{ext}(\underset{\sim}{q}, \omega) = v(\underset{\sim}{q}) \, n_e(\underset{\sim}{q}, \omega) . \tag{2.1.8}$$

$v(\underset{\sim}{q})$ is the Fourier transform of the Coulomb potential, i.e.,

$$v(\underset{\sim}{q}) = 4\pi e^2 / |\underset{\sim}{q}|^2 \quad , \quad q \neq 0 \, , \qquad (2.1.9)$$
$$= 0 \quad , \quad q = 0 \, .$$

The dielectric function for arbitrary values of q and ω is defined by,

$$\frac{1}{\epsilon(\underset{\sim}{q}, \omega)} = \frac{\hat{q} \cdot \underset{\sim}{E}(\underset{\sim}{q}, \omega)}{\hat{q} \cdot \underset{\sim}{D}(\underset{\sim}{q}, \omega)} = 1 + \frac{\bar{n}(\underset{\sim}{q}, \omega)}{n_e(\underset{\sim}{q}, \omega)} \qquad (2.1.10)$$

Then equations (2.1.7) and (2.1.8) alongwith equation (2.1.10) give,

$$\frac{1}{\epsilon(\underset{\sim}{q}, \omega)} = 1 + v(\underset{\sim}{q}) \chi^r(\underset{\sim}{q}, \omega) \qquad (2.1.11)$$

The response function $\chi^r(\underset{\sim}{q}, \omega)$ is related to the time dependent pair correlation function,

$$g(\underset{\sim}{r}, t) = \frac{1}{N} \int d\underset{\sim}{r}' \, \langle \rho(\underset{\sim}{r}', 0) \, \rho(\underset{\sim}{r}' + \underset{\sim}{r}, t) \rangle_{eq}$$

Hence, in turn it is related to the dynamic structure factor $S(\underset{\sim}{q}, \omega)$ (which is the Fourier transform in space and time of the pair correlation function) via,

$$\chi^r(\underset{\sim}{q}, \omega) = \left(\frac{n}{\hbar}\right) \int_{-\infty}^{\infty} d\omega' \, \frac{S(\underset{\sim}{q}, \omega') - S(-\underset{\sim}{q}, -\omega')}{\omega - \omega' + i\eta} \, . \qquad (2.1.12)$$

As shown by Van Hove[20], $S(\underset{\sim}{q}, \omega)$ has a definite description in the Born approximation theory, where the probability that the electron fluid absorbs a momentum $\hbar q$ and an energy $\hbar\omega$ by the scattering of an incident particle is given by

$$P(\underset{\sim}{q}, \omega) = n \, |v(\underset{\sim}{q})|^2 \, S(\underset{\sim}{q}, \omega) \, .$$

The equation (2.1.12) then yields,

$$\text{Im } \chi^r(\underset{\sim}{q}, \omega) = -\frac{n\pi}{\hbar} \{ S(\underset{\sim}{q}, \omega) - S(-\underset{\sim}{q}, -\omega) \} \, ,$$
$$= -\frac{n\pi}{\hbar} S(\underset{\sim}{q}, \omega) \, , \quad (\omega > 0) \, . \qquad (2.1.13)$$

since at T = 0 (to which we restrict ourselves throughout this thesis), the system only absorbs energy, the corresponding frequency has to be positive as taken in the above expressions. Equations (2.1.11) and (2.1.13) then give, the fluctuation dissipation theorem,

$$S(\underset{\sim}{q},\omega) = -\frac{\hbar q^2}{4\pi^2 n e^2}\,\mathrm{Im}\left(\frac{1}{\epsilon(\underset{\sim}{q},\omega)}\right). \qquad (2.1.14)$$

Thus, the dielectric function describes both, the time-dependent correlations between particles as well as the scattering properties. The static pair correlations also follow from the knowledge of $\epsilon(\underset{\sim}{q}, \omega)$. These are described by the static structure factor $S(\underset{\sim}{q})$ of X-ray diffraction theory,

$$S(\underset{\sim}{q}) = \int_0^\infty d\omega\, S(\underset{\sim}{q},\omega) \qquad (2.1.15)$$

or by the radial pair distribution function which is given by,

$$g(\underset{\sim}{r}) = 1 + \frac{1}{n}\int \frac{d^3q}{(2\pi)^3}\,\{S(\underset{\sim}{q}) - 1\}\, e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}. \qquad (2.1.16)$$

$g(\underset{\sim}{r})$ gives the probability of two electrons being found separated by a relative distance $\underset{\sim}{r}$ at any instant of time t.

The above considerations show that a detailed knowledge of $\epsilon(\underset{\sim}{q}, \omega)$ can give information about the dynamic and static correlations between the particles. Also $\epsilon(\underset{\sim}{q}, \omega)$ is directly related to experimentally measurable quantities.

We now define here the one particle and two particle Wigner distribution functions which are related to the density of the system and to the density-density correlation functions ; these are hence required for determination of the response

function and the dielectric function.

The one particle Wigner distribution function $f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)$ is defined as,

$$f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t) = \frac{1}{V}\int d^3x\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}} \left\langle \psi^{\dagger}_{\sigma}(\underset{\sim}{r}+\tfrac{\underset{\sim}{x}}{2},t)\,\psi_{\sigma}(\underset{\sim}{r}-\tfrac{\underset{\sim}{x}}{2},t)\right\rangle, \quad (2.1.17a)$$

where $\hat{\psi}$ is the field operator which can be written as,

$$\hat{\psi}_{\sigma}(\underset{\sim}{r},t) = \frac{1}{\sqrt{V}}\sum_{\underset{\sim}{k}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, a_{\underset{\sim}{k}\sigma}(t)$$

$a_{\underset{\sim}{k}\sigma}(t)$ is the annihiliation operator for an electron with momentum $\hbar k$ and spin σ. Similarly,

$$\hat{\psi}^{+}_{\sigma}(\underset{\sim}{r},t) = \frac{1}{\sqrt{V}}\sum_{\underset{\sim}{k}} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, a^{\dagger}_{\underset{\sim}{k}\sigma}(t)$$

$a^{+}_{\underset{\sim}{k}\sigma}(t)$ being the creation operator, $a_{\underset{\sim}{k}\sigma}$ and $a^{+}_{\underset{\sim}{k}\sigma}$ obey the usual anticommutation relations,

$$\left.\begin{aligned} &\{a_{\underset{\sim}{k}\sigma}(t),\, a^{\dagger}_{\underset{\sim}{k}'\sigma'}(t)\} = \delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\ ; \\ \text{and}\quad &\{a_{\underset{\sim}{k}\sigma}(t),\, a_{\underset{\sim}{k}'\sigma'}(t)\} = \{a^{\dagger}_{\underset{\sim}{k}\sigma}(t),\, a^{\dagger}_{\underset{\sim}{k}'\sigma'}(t)\} = 0\ . \end{aligned}\right\} \quad (2.1.18)$$

The space Fourier transform of $f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)$ can then be written in terms of $a_{\underset{\sim}{k}\sigma}$ and $a^{+}_{\underset{\sim}{k}\sigma}$ as,

$$f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \left\langle a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t)\right\rangle . \quad (2.1.17b)$$

The density operator $\hat{\rho}(\underset{\sim}{r},t)$ is given by,

$$\hat{\rho}(\underset{\sim}{r},t) = \sum_{\sigma} \psi^{\dagger}_{\sigma}(\underset{\sim}{r},t)\,\psi_{\sigma}(\underset{\sim}{r},t)\ . \quad (2.1.19a)$$

Its space Fourier transform is thus given by,

$$\hat{\rho}(\underset{\sim}{q},t) = \sum_{\underset{\sim}{k}\sigma} a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t)\ . \quad (2.1.19b)$$

Then from equations (2.1.17b) and (2.1.19b) we have,

$$\langle\hat{\rho}(\underset{\sim}{q},t)\rangle = \sum_{\underset{\sim}{k}\sigma} f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\ .$$

In real space, we then have,

$$n(\underset{\sim}{r},t) = \langle\hat{\rho}(\underset{\sim}{r},t)\rangle = \sum_{\underset{\sim}{k}\sigma} f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)\ . \quad (2.1.20)$$

In equilibrium, the left hand side of the above equation just

gives the constant density n = N/v where N is the total number of particles in the system. This implies that the equilibrium value of the one particle function is given by,

$$f^{(1)eq}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) = \delta_{\underset{\sim}{q},0}\, n_{\underset{\sim}{k}\sigma} , \qquad (2.1.21)$$

where, $$n_{\underset{\sim}{k}\sigma} = \langle a^{\dagger}_{\underset{\sim}{k}\sigma} a_{\underset{\sim}{k}\sigma} \rangle_{eq} .$$

$n_{\underset{\sim}{k}\sigma}$ refers to the interacting system but in practice it is usually replaced by $n^{o}_{\underset{\sim}{k}\sigma}$, the momentum distribution function (i.e. the Fermi function) for a non-interacting system. We also use $n^{o}_{\underset{\sim}{k}\sigma}$ for $n_{\underset{\sim}{k}\sigma}$ in our numerical work. We write $f^{(1)}$ as a sum of $f^{(1)eq}$ (its value at equilibrium, i.e. in the absence of an external field), and $\bar{f}^{(1)}$ (its deviation from equilibrium),

$$f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = f^{(1)eq}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) + \bar{f}^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) .$$

We note here that henceforth any barred quantity denotes deviation of that quantity from its equilibrium value. Writing a similar equation for the density $n(\underset{\sim}{q},t)$,

$$n(\underset{\sim}{q},t) = n\,\delta_{\underset{\sim}{q},0} + \bar{n}(\underset{\sim}{q},t) ,$$

we have,

$$\bar{n}(\underset{\sim}{q},t) = \sum_{\underset{\sim}{k}\sigma} \bar{f}^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) . \qquad (2.1.22)$$

We now introduce the two particle Wigner distribution function

$$f^{2}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t) = \frac{1}{V^2}\int d^3x\, d^3x'\; e^{i\underset{\sim}{k}\cdot\underset{\sim}{x}}\; e^{i\underset{\sim}{k}'\cdot\underset{\sim}{x}'}$$
$$\cdot \langle \psi^{\dagger}_{\sigma}(\underset{\sim}{r}+\tfrac{\underset{\sim}{x}}{2},t)\,\psi^{\dagger}_{\sigma'}(\underset{\sim}{r}'+\tfrac{\underset{\sim}{x}'}{2},t)\,\psi_{\sigma'}(\underset{\sim}{r}'-\tfrac{\underset{\sim}{x}'}{2},t)\,\psi_{\sigma}(\underset{\sim}{r}-\tfrac{\underset{\sim}{x}}{2},t)\rangle ,$$

which can be written in Fourier space as,

$$f^{2}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t) = \langle a^{\dagger}_{\underset{\sim}{k}-\frac{\underset{\sim}{q}}{2}\sigma}(t)\, a^{\dagger}_{\underset{\sim}{k}'-\frac{\underset{\sim}{q}'}{2}\sigma}(t)\, a_{\underset{\sim}{k}'+\frac{\underset{\sim}{q}'}{2}\sigma'}(t)\, a_{\underset{\sim}{k}+\frac{\underset{\sim}{q}}{2}\sigma}(t)\rangle . \qquad (2.1.23)$$

Next we define the irreducible distribution function denoted by $f^{(2)}$ as,

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t) = f^{2}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t) - f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t) . \quad (2.1.24)$$

As done for the case of the one particle function, here also we can write both $f^{(2)}$ and f^{2} as sums of the equilibrium values and the deviations from equilibrium. The two particle function is related to the density-density correlation function $D^2(\underset{\sim}{q},\underset{\sim}{q}',t)$ which is defined as,

$$D^2(\underset{\sim}{q},\underset{\sim}{q}',t) = \langle \hat{\rho}(\underset{\sim}{q},t)\,\hat{\rho}(\underset{\sim}{q}',t)\rangle \quad (2.1.25)$$

The irreducible density-density correlation function is given by,

$$\begin{aligned} D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t) &= \langle \hat{\hat{\rho}}(\underset{\sim}{q},t)\,\hat{\hat{\rho}}(\underset{\sim}{q}',t)\rangle , \\ &= \langle [\hat{\rho}(\underset{\sim}{q},t) - \langle\hat{\rho}(\underset{\sim}{q},t)\rangle][\hat{\rho}(\underset{\sim}{q}',t) - \langle\hat{\rho}(\underset{\sim}{q}',t)\rangle]\rangle , \\ &= \langle \hat{\rho}(\underset{\sim}{q},t)\,\hat{\rho}(\underset{\sim}{q}',t)\rangle - \langle\hat{\rho}(\underset{\sim}{q},t)\rangle\langle\hat{\rho}(\underset{\sim}{q}',t)\rangle , \\ &= D^2(\underset{\sim}{q},\underset{\sim}{q}',t) - \langle\hat{\rho}(\underset{\sim}{q},t)\rangle\langle\hat{\rho}(\underset{\sim}{q}',t)\rangle . \end{aligned} \quad (2.1.26)$$

If we define two functions $C^2(\underset{\sim}{q},\underset{\sim}{q}',t)$ and $C^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t)$ as,

$$C^{(2)}_{2}(\underset{\sim}{q},\underset{\sim}{q}',t) = \sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} f^{(2)\sim}_{2\,\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t),$$

we find the relation between the functions $D^{(2)}$ and $C^{(2)}$ to be,

$$D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t) = C^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t) + \langle\hat{\rho}(\underset{\sim}{q}+\underset{\sim}{q}',t)\rangle . \quad (2.1.27)$$

A similar relation is observed between D^2 and C^2 also.

The equilibrium value for $f^{(2)}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma}(\underset{\sim}{q},\underset{\sim}{q}',t)$ is usually not known but it satisfies an exact condition which can be obtained from the equilibrium value of the density-density correlation function, denoted by $D^{(2)eq}$. To obtain an expression for $D^{(2)eq}$ in terms of the equilibrium pair correlation function $g(\underset{\sim}{r})$, we work in the real space and start with the density

operator as,

$$\hat{\delta}(\underset{\sim}{r}, t) = \sum_{i=1}^{N} \delta(\underset{\sim}{r} - \underset{\sim}{r}_i(t)),$$

where $\underset{\sim}{r}_i(t)$ is the position operator (in the Heisenberg representation) for the ith electron in the system of N electrons. Alternatively,

$$\delta(\underset{\sim}{r}) = \frac{1}{V} \sum_{\underset{\sim}{q}} e^{i\underset{\sim}{q}.\underset{\sim}{r}} .$$

Then,

$$D^{2eq}(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{1}{V^2} \sum_{\underset{\sim}{q},\underset{\sim}{q}'} \left\langle \sum_{i,j=1}^{N} e^{i\underset{\sim}{q}.(\underset{\sim}{r} - \underset{\sim}{r}_i(t))} \, e^{i\underset{\sim}{q}'.(\underset{\sim}{r}' - \underset{\sim}{r}_j(t))} \right\rangle . \quad (2.1.28)$$

In equilibrium, since the $\underset{\sim}{r}_i$ and $\underset{\sim}{r}$ are at the same instant of time t, we drop the index t and in this case they commute so that the exponents can be added algebraically. Also for a homogeneous system that we are considering, $D^{2eq}(\underset{\sim}{r},\underset{\sim}{r}')$ must be independent of the choice of the origin so that $D^{2eq}(\underset{\sim}{r},\underset{\sim}{r}') = D^{2eq}(|r - r'|)$. Hence,

$$D^{2eq}(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{1}{V^2} \sum_{\underset{\sim}{q},\underset{\sim}{q}'} \left[\sum_{i} \left\langle e^{i\underset{\sim}{q}.(\underset{\sim}{r} - \underset{\sim}{r}')} \right\rangle_{eq} + \sum_{i \neq j=1}^{N} \left\langle e^{i\underset{\sim}{q}.(\underset{\sim}{r} - \underset{\sim}{r}' + \underset{\sim}{r}_j - \underset{\sim}{r}_i)} \right\rangle_{eq} \right] \delta_{\underset{\sim}{q}+\underset{\sim}{q}',0} ,$$

$$= \frac{N}{V^2} \sum_{\underset{\sim}{q}} e^{i\underset{\sim}{q}.(\underset{\sim}{r} - \underset{\sim}{r}')} + \frac{1}{V^2} \sum_{\underset{\sim}{q}} \sum_{i \neq j=1}^{N} \left\langle e^{i\underset{\sim}{q}.(\underset{\sim}{r} - \underset{\sim}{r}' - \underset{\sim}{r}_i + \underset{\sim}{r}_j)} \right\rangle_{eq} ,$$

$$= n\,\delta(\underset{\sim}{r} - \underset{\sim}{r}') + n^2 g(\underset{\sim}{r} - \underset{\sim}{r}') . \quad (2.1.29a)$$

where we have used the usual definition of the radial distribution function[5],

$$n g(\underset{\sim}{r}) = \frac{1}{N} \sum_{i \neq j=1}^{N} \left\langle \delta(\underset{\sim}{r} + \underset{\sim}{r}_j - \underset{\sim}{r}_i) \right\rangle_{eq} . \quad (2.1.30)$$

Using the relation between the reducible and irreducible density-density correlation function, (equation (2.1.26)),

we have,

$$D^{(2)eq}(\underset{\sim}{r},\underset{\sim}{r}') = n\,\delta(\underset{\sim}{r}-\underset{\sim}{r}') + n^2\{g(\underset{\sim}{r}-\underset{\sim}{r}')-1\}. \qquad (2.1.29b)$$

In Fourier space then, (using equation (2.1.16)),

$$D^{2eq}(\underset{\sim}{q},\underset{\sim}{q}') = \delta_{\underset{\sim}{q}+\underset{\sim}{q}',0}\,[N^2\delta_{\underset{\sim}{q},0} + N\,S(\underset{\sim}{q})]\;; \qquad (2.1.31a)$$

and $$D^{(2)eq}(\underset{\sim}{q},\underset{\sim}{q}') = \delta_{\underset{\sim}{q}+\underset{\sim}{q}',0}\,N\,S(\underset{\sim}{q}). \qquad (2.1.31b)$$

From equation (2.1.27), we have expressions for C^{2eq} and $C^{(2)eq}$ in both real and Fourier space. These are given by,

$$C^{2eq}(\underset{\sim}{r},\underset{\sim}{r}') = n^2 g(\underset{\sim}{r}-\underset{\sim}{r}')\;; \qquad (2.1.32a)$$

$$C^{(2)eq}(\underset{\sim}{r},\underset{\sim}{r}') = n^2\{g(\underset{\sim}{r}-\underset{\sim}{r}')-1\}\;; \qquad (2.1.32b)$$

$$C^{2eq}(\underset{\sim}{q},\underset{\sim}{q}') = \delta_{\underset{\sim}{q}+\underset{\sim}{q}',0}\,[N^2\delta_{\underset{\sim}{q},0} + N\{S(\underset{\sim}{q})-1\}]\;; \qquad (2.1.32c)$$

$$C^{(2)eq}(\underset{\sim}{q},\underset{\sim}{q}') = \delta_{\underset{\sim}{q}+\underset{\sim}{q}',0}\,N\{S(\underset{\sim}{q})-1\}. \qquad (2.1.32d)$$

Finally we define a time-ordered or causal density-density response function,

$$\chi^c(\underset{\sim}{r},\underset{\sim}{r}';t-t') = (i\hbar)^{-1}\langle T\{\hat{\tilde{\rho}}(\underset{\sim}{r},t)\hat{\tilde{\rho}}(\underset{\sim}{r}',t')\}\rangle_{eq}, \qquad (2.1.33)$$

where,

$$\hat{\tilde{\rho}}(\underset{\sim}{r},t) = \hat{\rho}(\underset{\sim}{r},t) - \langle\hat{\rho}(\underset{\sim}{r},t)\rangle_{eq}.$$

The causal function is related to the retarded function as, (see Appendix I),

$$\mathrm{Re}\,\chi^c(\underset{\sim}{q},\omega) = \mathrm{Re}\,\chi^r(\underset{\sim}{q},\omega)\;; \qquad (2.1.34a)$$

and $$\mathrm{sgn}(\omega)\,\mathrm{Im}\,\chi^c(\underset{\sim}{q},\omega) = \mathrm{Im}\,\chi^r(\underset{\sim}{q},\omega). \qquad (2.1.34b)$$

The equilibrium value of the density-density correlation function can be written in terms of the response functions as (see Appendix I),

$$D^{(2)eq}(\underset{\sim}{q},-\underset{\sim}{q}) = \lim_{t'\to t} i\hbar\,\chi^c(\underset{\sim}{q},t-t'),$$

$$= \oint \frac{d\omega'}{2\pi} i\hbar V \chi^c(q, \omega') , \qquad (2.1.35a)$$

$$= -\frac{\hbar V}{\pi} \int_0^\infty d\omega' \ \mathrm{Im}\, \chi^r(q, \omega') . \qquad (2.1.35b)$$

To express it in terms of the retarded function we have first used the spectral representation for the causal function (also derived in Appendix I), i.e.,

$$\chi^c(q, \omega) = -\frac{1}{\pi} \int_0^\infty d\omega' \ \mathrm{Im}\, \chi^c(q, \omega') \left\{ \frac{1}{\omega - \omega' + i\delta} - \frac{1}{\omega + \omega' - i\delta} \right\} , \qquad (2.1.36)$$

and then the relation between the imaginary parts of the retarded and time-ordered functions (equation (2.1.34b)). Using the expression for $D^{(2)eq}(q, -q)$ and then the definition of $S(q)$ (equation (2.1.15)), we get back the relation between the dynamic structure factor $S(q,\omega)$ and $\mathrm{Im}\, \chi^r(q,\omega)$, i.e.

$$S(q, \omega) = -\frac{\hbar}{n\pi} \mathrm{Im}\, \chi^r(q, \omega) .$$

Before we proceed further we would like to state here that we work with atomic units in all our calculations, i.e., we take $\hbar = 1$; m_e , the electron mass $= 1/2$; $e^2 = 2$ and a_o , the Bohr radius $= 1$. The energy in this case is in units of Rydberg. In these units then, the Fermi momentum $q_F = 1/\alpha r_s$ and the Fermi energy $\epsilon_F = 1/(\alpha r_s)^2$, where r_s is a dimensionless quantity defined through the relation,

$$n = (4\pi r_s^3 / 3)^{-1} . \qquad (2.1.37)$$

Here n is the constant density of electrons in the system. For metallic densities, we have $1.8 \leq r_S \leq 5.6$. In these units, the usual classical plasma (or plasmon) frequency ω_p is given by,

$$\frac{\omega_p}{\epsilon_F} = \left(\frac{16 \alpha r_s}{3\pi} \right)^{1/2} , \qquad (2.1.38)$$

where $\alpha = (4 / 9\pi)^{1/3} = 0.521$.

2.2 EXACT SUM RULES

The exact behaviour of the response function for certain limiting conditions is known. These limiting conditions, arising out of behaviour at long wavelength or in the static limit, thus provide a good check on a theory. Below we list a few of these limiting conditions.

2.2.1 Positivity of $g(\underset{\sim}{r})$

The radial distribution function $g(\underset{\sim}{r})$, being defined as the probability of finding two particles in equilibrium separated by a relative distance $\underset{\sim}{r}$, should remain positive for all values of r.

2.2.2 Moment sum rules

These are a set of sum rules which refer to the short time behaviour of the response function i.e., the high frequency behaviour[2] of $\chi(\underset{\sim}{q},\omega)$. The function $\chi(\underset{\sim}{q},\omega)$ can be written as,

$$\chi(\underset{\sim}{q},\omega) = \int_0^\infty dt\ \Phi(\underset{\sim}{q},t)\ e^{-i\omega t},$$

with,

$$\Phi(\underset{\sim}{q},t) = -\frac{1}{i\pi}\int d^3r\ \langle [\hat{\rho}(0,0),\hat{\rho}(\underset{\sim}{r},t)]_- \rangle\ e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}.$$

The quantity $\Phi(\underset{\sim}{q},t)$ is an odd function of time so that we can invert the previous equation and write,

$$\Phi(\underset{\sim}{q},t) = -\frac{1}{i\pi}\int_{-\infty}^{\infty} d\omega\ \mathrm{Im}\,\chi(\underset{\sim}{q},\omega)\ e^{i\omega t}.$$

The time derivatives of $\Phi(\underset{\sim}{q},t)$ at t = 0, if they exist, are then given by,

$$\left.\frac{d^{(2n+1)}\,\Phi(\underset{\sim}{q},t)}{dt^{(2n+1)}}\right|_{t=0} = -(-1)^n \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\, \omega^{2n+1}\, \mathrm{Im}\,\chi(\underset{\sim}{q},\omega),$$

$$= (-1)^n\, M_{2n+1}(\underset{\sim}{q}) \,.$$

The moment sum rules thus require that the odd moments of the dissipation spectrum be equal to the static correlations of the system at equilibrium. The above expression can also be stated as,

$$\langle \omega^l \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{\pi}\, \omega^l\, \mathrm{Im}\,\chi(\underset{\sim}{q},\omega) = -M_l(\underset{\sim}{q}) \qquad (2.2.1)$$

where,

$$M_l(\underset{\sim}{q}) = \frac{1}{n\hbar V}\left(i\frac{\partial}{\partial t}\right)^l \langle [\hat{\rho}(\underset{\sim}{q},t)\,,\,\hat{\rho}^{+}(\underset{\sim}{q},0)]_{-}\rangle\Big|_{t=0} \qquad (2.2.2)$$

The first few moments have been explicitly evaluated using the commutation properties of the density operators to determine the static correlations.

(i) The first moment sum rule states that,

$$\langle \omega \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \cdot \omega\ \mathrm{Im}\,\chi(\underset{\sim}{q},\omega) = -M_1(\underset{\sim}{q}) \qquad (2.2.3a)$$

where,

$$M_1(\underset{\sim}{q}) = -\frac{1}{V} \langle [[H\,,\,\hat{\rho}(\underset{\sim}{q},t)]_{-}\,,\,\hat{\rho}^{+}(\underset{\sim}{q},0)]_{-}\rangle\Big|_{t=0},$$

$$= nq^2/m_e \,. \qquad (2.2.3b)$$

This is the so called oscillator strength sum rule for the electron gas, and most theories set forth for the dielectric function satisfy this sum rule.

(ii) For the third moment sum rule one needs to evaluate $M_3(\underset{\sim}{q})$. The expression for the third moment was first given by Puff[21] and later used by Pathak and Vashishta[22] and is

given by,

$$M_3(\underset{\sim}{q}) = \frac{nq^2}{m_e}\left\{\omega_p^2 + \frac{2q^2}{m_e}\langle KE\rangle + \left(\frac{\hbar q^2}{2m_e}\right)^2 - \omega_p^2\, G^{\infty}(q)\right\}, \qquad (2.2.4a)$$

where,

$$G^{\infty}(q) = -\frac{3}{4}\int_0^{\infty} dq'\; q'^2 \left\{S(q') - 1\right\}\left\{\frac{5}{6} - \frac{q'^2}{2q^2} + \frac{(q^2 - q'^2)^2}{4q^3 q'} \ln\left|\frac{q+q'}{q-q'}\right|\right\}. \qquad (2.2.4b)$$

Here $G^{\infty}(q)$ has been written in reduced units (i.e. where q is in q_F and $\hbar\omega$ in ϵ_F). $\langle K.E\rangle$ in (2.2.4a) refers to the average kinetic energy per electron in the interacting system and ω_p is the plasmon frequency given by (2.1.38).

(iii) An expression for the fifth moment has been given by Forster et al.[23]. Investigations by Family[24] however indicate that the fifth moment may diverge for the degenerate electron fluid over the range of r_s for which $g(\underset{\sim}{r} = 0) \neq 0$. Hence care should be taken while using the fifth moment sum rule in case of metallic systems.

2.2.3 Compressibility sum rule

The ratio of the compressibility of an interacting system (K) to that of the free electron gas (K_f), i.e., K/K_f, is related to the static, long wavelength limit of the dielectric function $\epsilon(\underset{\sim}{q},\omega)$[25], i.e.,

$$\lim_{q\to 0} \epsilon(q, 0) = 1 + \frac{q_{TF}^2}{q^2}\cdot\frac{K}{K_f}, \qquad (2.2.5)$$

where q_{TF} is the Thomas-Fermi wavevector given by

$q_{TF} = (3\alpha/\sqrt{r_s})q_F$ with $\alpha = (4/9\pi)^{1/3}$. The quantum mechanical virial theorem also provides with an easy method for obtaining an expression for the compressibility ratio K/K_f for a system of electrons interacting via Coulomb potential $v(\underset{\sim}{r})$ in the presence of a rigid positive background[26]. The pressure of the system can be written as

$$p = \frac{2}{3}\left(n\langle KE\rangle + \frac{n}{2}\langle PE\rangle\right), \qquad (2.2.6)$$

where $\langle KE\rangle$ and $\langle PE\rangle$ are respectively the expectation values of the kinetic energy and the potential energy per particle in the ground state and n is the number density. The compressibility is defined as,

$$\frac{1}{K} = n\,\frac{\partial p}{\partial n} \quad . \qquad (2.2.7)$$

Expressing the potential energy in terms of the equilibrium pair correlation function and differentiating equation (2.2.6) with respect to n, we have,

$$\left(\frac{K_f}{K}\right)_V = \frac{1}{n\epsilon_F}\left[n\,\frac{\partial}{\partial n}(n\langle KE\rangle) + \frac{n^2}{2}\int d\underset{\sim}{x}\; v(\underset{\sim}{x})\,.\right.$$

$$\left.\left(\{g(\underset{\sim}{x},n) - 1\} + \frac{n}{2}\,\frac{\partial}{\partial n}\{g(\underset{\sim}{x},n) - 1\}\right)\right]. \qquad (2.2.8)$$

Here $K_f = (n\epsilon_f)^{-1}$; subscript V refers to the calculations using virial theorem and the potential energy is given by,

$$\langle PE\rangle = \frac{n}{2}\int d\underset{\sim}{x}\; v(\underset{\sim}{x})\{g(\underset{\sim}{x},n) - 1\} \quad . \qquad (2.2.9)$$

The compressibility sum rule states that the ratio of the compressibilities obtained from the static, small q limit of the dielectric function, i.e., from equation (2.2.5), should be

the same as that obtained using the virial theorem, i.e. from equation (2.2.8).

2.2.4 Dispersion and damping of plasmons

The plasmon spectrum is given by the relation

$$\epsilon(\underset{\sim}{q}, \omega) = 0 \qquad (2.2.10)$$

For example, for $q \to 0$, the solution of (2.2.10) is,

$$\omega(q) = \omega_p + \alpha q^2 + i\gamma q^2 + O(q^4), \qquad (2.2.11)$$

which follows from perturbative calculations[7]. α and γ are called the dispersion and damping coefficients respectively. Plasmon-decay into single pair excitations is allowed by the conservation laws only above a cut-off wavenumber $q_c \sim \omega_p/v_F$, due to the sharp drop of the ground state momentum distribution at the Fermi surface. Multipair processes are however operative at all non-vanishing momentum and so lead to a non-zero plasmon lifetime[7].

2.3 REVIEW OF EARLIER THEORIES

One of the earliest attempts made in studying the response of an electron gas system has been through the time-dependent Hartree approximation, commonly known as the random phase approximation (abbreviated as RPA). Here it is assumed that the electrons respond as free particles to an effective time-dependent mean field which is the sum of the external field and the field due to the induced density of the system[2]. Thus all the exchange and correlation effects between the

electrons are approximated by the self-consistent average field of all the electrons moving together. In this approach then we have,

$$\chi^r(\underset{\sim}{q},\omega) = \frac{\chi^{ro}(\underset{\sim}{q},\omega)}{1 - v(q)\,\chi^{ro}(\underset{\sim}{q},\omega)}, \qquad (2.3.1)$$

and

$$[\epsilon^r(\underset{\sim}{q},\omega)]^{-1} = 1 - v(\underset{\sim}{q})\,\chi^{ro}(\underset{\sim}{q},\omega) = 1 + Q^{ro}(\underset{\sim}{q},\omega).$$

χ^{ro} is the free particle response function ; $Q^r(\underset{\sim}{q},\omega) = -v(\underset{\sim}{q})\,\chi^r(\underset{\sim}{q},\omega)$ is called the polarisability of the system and $Q^{ro}(\underset{\sim}{q},\omega)$ here refers to the free electron polarisability or the Lindhard polarisability[27]. It is given by,

$$Q^{ro}(\underset{\sim}{q},\omega) = -v(\underset{\sim}{q})\cdot\frac{1}{V}\sum_{\underset{\sim}{k}\sigma}\frac{n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n^0_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}}{\hbar\omega + i\delta - \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})}. \qquad (2.3.2)$$

We give here for future reference also, the real and imaginary parts of this function expressed in reduced units[28] (momenta and energy in units of q_F and ϵ_F respectively).

$$\mathrm{Re}\,Q^{ro}(q,\omega) = \frac{d\gamma_s}{q^3}\left[2q - \left\{1 - \left(\frac{\omega}{2q} - \frac{q}{2}\right)^2\right\}\ln\left|\frac{\omega + 2q - q^2}{\omega - 2q - q^2}\right| + \left\{1 - \left(\frac{\omega}{2q} + \frac{q}{2}\right)^2\right\}\ln\left|\frac{\omega + 2q + q^2}{\omega - 2q + q^2}\right|\right] \qquad (2.3.3)$$

and

$$\mathrm{Im}\,Q^{ro}(q,\omega) = \frac{d\gamma_s}{\pi q^3}\left\{1 - \left(\frac{\omega}{2q} - \frac{q}{2}\right)^2\right\}, \quad \text{for } q \le 2 \;\&\; 2q - q^2 < \omega < 2q + q^2$$

$$q > 2 \;\&\; q^2 - 2q < \omega < 2q + q^2$$

$$= \frac{d\gamma_s}{\pi q^3}\cdot\frac{\omega}{q}, \quad q \le 2 \;\&\; 0 < \omega < 2q - q^2$$

$$= 0, \quad \text{otherwise}. \qquad (2.3.4)$$

This simple approximation gives the basic features of the excitations of the interacting electron system (e.g., plasmons and particle-hole pairs), but takes proper account of only the

long range Coulomb interaction via screening. Thus it is seen that RPA does not satisfy compressibility sum rule. Also the value of pair correlation function g(r) in this case is negative for small r over the entire metallic density region. Hence, though the RPA succeeds in explaining some of the metallic properties, it fails to describe correctly the short range effects.

Efforts have been made over the past two decades to give theories that go beyond the RPA, using different theoretical approaches. Most of these theories try to take into account the fact that due to the short range exchange and correlation effects, there is a local depletion in the density around each electron, i.e., there exists an exchange-correlation hole around each electron. This leads to a modification of the time-dependent Hartree mean field and one refers to the difference between this effective field and the mean Hartree field via the so called local field correction, $G(\underset{\sim}{q},\omega)$. Earlier theories assumed that the local field was a real, static quantity. This amounts to assuming that the electrons move with their exchange-correlation holes held rigidly to them.

One of the earliest workers in this direction has been Hubbard[28]. From a diagrammatic point of view, since RPA corresponds to only the empty electron hole bubble diagram[29], Hubbard included the leading exchange diagrams and in a certain approximation was able to sum the infinite set of ladder diagrams. The result obtained is a modification to the mean field via a static field G(q) which tends to 1/2 for

$q \to 0$, implying that the exchange terms taken cancel half of the Coulomb interaction in this limit. Physically, therefore this amounts to assuming the presence of an exchange hole around the electron. Other workers like Geldart and Vosko[30], have tried to improve upon this static local field by empirically including the correlation effects via a parameter. The parameter was then evaluated by requiring that the compressibility sum rule be satisfied. The importance of including the correlation effects was stressed by these studies.

An important and significant contribution to these mean field approaches has come from Singwi and co-workers[2,6,31,32]. They have used the equation of motion method. The equation of motion for the one particle Wigner distribution function $f^{(1)}$ contains the two particle Wigner function $f^{(2)}$; the two particle equation of motion contains $f^{(3)}$ and so on, thus giving a set of coupled equations, which is the quantum analog of the classical Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy of equations[5,33] . The equation of motion method involves truncation of this series by approximating for the higher order distribution function and solving the resultant, simplified integral equations. Singwi et al (STLS)[31] in a rather intuitive manner, truncated the series by approximating for $\bar{f}^{(2)}$ in the first equation of motion, via the equilibrium pair correlation function g(r). They used,

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}, \underset{\sim}{r}', t) = f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r}, t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}', t)\{g(\underset{\sim}{r}-\underset{\sim}{r}')-1\} \qquad (2.3.5)$$

The resultant expression for static local field $G(\underset{\sim}{q})$ contains the static structure factor $S(\underset{\sim}{q})$ and can be solved self-consistently with the fluctuation dissipation theorem (equations (2.1.13) to (2.1.15)). There was a great improvement in $g(\underset{\sim}{r})$ values over the earlier theories. For example, $g(\underset{\sim}{r})$ is found to be positive here even for $r \to 0$ for $r_s > 4$. It is worthwhile to note here that if the $S(\underset{\sim}{q})$ is replaced by its Hartree-Fock value, i.e., the $S(\underset{\sim}{q})$ for a non-interacting system, we get back the result obtained by Hubbard.

Later Singwi et al. (SSTL)[6], used another approximation for $f^{(2)}$ (in particular for $\bar{f}^{(2)}$) which was obtained by making an ad-hoc approximation for the vertex like function occurring in an integral equation for the corresponding time-ordered function. This approximation includes the dynamic screening effect but the local field eventually derived by SSTL was still static. In this approximation, the compressibility sum rule was nearly satisfied without much harm to the $g(\underset{\sim}{r})$ values. In principle, this method includes the dynamics of the hole and should lead to a dynamic local field correction but SSTL[6] have investigated only the static case. In order to improve the STLS[31] theory so that it gives a better agreement for the compressibility sum rule, Vashishta and Singwi[32] included the variation of the pair correlation function $g(\underset{\sim}{r})$ with the electron density n. They thus obtained,

$$G^{VS}(\underset{\sim}{q}) = \left(1 + \alpha \frac{\partial}{\partial n}\right)\left\{-\frac{1}{n}\int \frac{d^3q'}{(2\pi)^3} \frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}\left[S(\underset{\sim}{q}-\underset{\sim}{q}', n) - 1\right]\right\}, \quad (2.3.6)$$

with the requirements that the static structure factor S(q) and the parameter a be determined self-consistently with the fluctuation dissipation theorem (as in the earlier cases) and the compressibility sum rule respectively. The calculation yielded $a = \frac{2}{3}$ for all r_s in the metallic density range. In fact 'a' is found to be a slowly increasing function of r_s tending to a value of 1/2 for $r_s \rightarrow 0$[34]. The g(r) values in this scheme agree quite well with the earlier results. Comparing the compressibility obtained here with the exact isothermal compressibility, Vaishya and Gupta[35] have further justified the value of 'a' obtained by Vashishta and Singwi[32]. We note here that the quantity in the curly bracket in equation (2.3.6) is the local field obtained by STLS[31].

The static local field has also been obtained by Ichimaru[33] and Totsuji and Ichimaru[36], who solved the equation of motion for the two particle function by decoupling the three particle distribution function into the equilibrium correlation functions using the convolution approximation. Thus they obtained a static local field expressed as a functional of the static structure factor which can be calculated using the same self-consistent scheme as suggested by Singwi et al[31]. This method gives very good agreement with the compressibility sum rule.

Geldart and Taylor[37] have used the diagrammatic perturbation theory to give a systematic study for the static dielectric function. Following the earlier work of Geldart and

Vosko[30] and Geldart[38], they first considered the lowest order Hartree - Fock contributions and calculated numerically the static response of the system. They later considered the higher order exchange and correlation diagrams also,to give an interpolation formula for the wavenumber and density dependence of the static dielectric function.

All these theories which give a static local field correction are however neither able to give an expression for the damping of long wavelength plasmons nor are they able to satisfy higher order moment sum rules. For these it is necessary to have a complex, frequency dependent local field correction. A dynamic local field correction corresponds to the dynamic motion of the hole around each electron. The assumption of a rigid hole (made while calculating static local field) is valid only for a slowly varying perturbing force. In case the external force is rapidly varying, the hole distorts appreciably and also performs dynamic motion with respect to the electron. To include these effects then it is essential to have a complex, dynamic local field correction. Recent X-ray and energy loss experiments[4] have further emphasised the need to develop such a dynamic local field.

Eoth X-ray and energy loss experiments have been performed to measure energy loss over a wide range of momentum transfers. At large momentum transfers ($\sim 2q_F$), these scattering experiments yield unexpected results[39,40]. The ecitation

spectrum obtained has a double peak structure with a broad shoulder appearing on the high frequency side of the main peak. For q slightly lower than $2q_F$, the former is of lower strength than the latter ; at $q \simeq 2q_F$ the 'switching over' of the two strengths takes place and for still higher $q(>2q_F)$, the former exists as a single broad peak corresponding to free particle excitations. In the whole range of $q_c < q < 2q_F$ (q_c here corresponds to the critical wavevector at which the plasmon joins the particle hole continuum), this peak does not show any dispersion. These features have been exhibited by such diverse systems as Al, Be and graphite that the origin is considered to be in the correlation and exchange effects rather than in the band structure effects. None of the earlier theories (discussed so far), giving a static local field correction, have been able to reproduce the experimental results. Hence inclusion of dynamic and dissipative effects to give a dynamic local field correction is essential.

One of the earlier theories for a dynamic local field correction is the one suggested by Toigo and Woodruff[41]. Their method is based on the equations of motion for the Green's functions and involves decoupling approximations that are constrained by the moment sum rules. The equilibrium two particle function is an unknown quantity here and additional approximations of the Hartree Fock type have been used for it. Dynamical exchange effects were also included by Brosens et al[42,43]

who decoupled the equation of motion for the Wigner distribution function using Hartee-Fock prescription. They then solved the linearised equation using the variational method. They obtained a frequency dependent local field and also observed a logarithmic singularity in it at certain characteristic frequencies given by $\omega = |q \pm q^2/2|$ and hence felt that the frequency dependence of the local field plays a very important role and should not be neglected. Following a more or less similar approach, Tripathi and co-workers[44] also reported a frequency dependent local field correction but with no singularities in its value. Their numerical work is however erroneous and has been discussed in great detail by Holas et al [9].

Another theory which displays these logarithmic singularities is the first order perturbation theory investigated by Holas et al[9] who carried out the dynamic calculations along the same lines as the static first order perturbation calculations of Geldart and Taylor[37]. The density-density response function in this case is a sum of the free particle response function χ^0 and the function χ^1, the latter having the contributions from both, the self energy corrections and the exchange local field. The imaginary part of χ^1 shows discontinuities at the same frequencies as observed by Brosens and co-workers[42,43]. This leads to logarithmic singularities in the real part of χ^1 at these frequencies. Holas et al. noticed that the singularities could be rounded off if the

self energy contribution was evaluated to all orders. These calculations give good results for the pair correlation function and the dispersion coefficient but one is not able to observe the damping of plasmons or the high frequency tail in the dynamic structure factor. A similar perturbation series expansion had been suggested by Dharma-Wardana[45] but no attempt so far has been made to evaluate it.

There have been various equation of motion studies also to obtain a frequency dependent local field correction. Hasegawa and Shimizu[46] have carried out a totally quantum mechanical treatment of the equation of motion for the one particle Wigner distribution function using the same decoupling scheme as suggested and employed by STLS[31]. The local field correction in this case was frequency dependent. The $g(\underset{\sim}{r})$ values calculated were positive for all distances r in the whole metallic density range. The compressibility sum rule was still not satisfied though there was an improvement over the corresponding STLS[31] result. The damping of plasmons is finite here but we find that it varies as q^5 in the $q \rightarrow 0$ limit, unlike the expected q^2 behaviour.

Niklasson[8] has also used the equation of motion approach, where he truncated the series of equations at the equation of motion for the two particle distribution function. The exact behaviour at high frequencies or for large wavevectors has been investigated. The high frequency expansion for the local field

was shown to satisfy the third moment sum rule exactly, i.e., it had the same form for $G^{\infty}(q)$, as in equation (2.2.4b) for the third moment. Seeing the drastic frequency dependence of the local field at large wavevectors, Niklasson also stressed the need to have a dynamic local field which would include the dynamics of the hole surrounding the electron.

Aravind et al[10] have also truncated the equation of motion for $f^{(2)}$ by making an RPA like approximation for the two particle function. The $G(q,\omega)$ obtained includes both, the results obtained earlier by the same authors using first order perturbation theory[9] and the high frequency and large wavevector results obtained by Niklasson[8]. The singularities at characteristic frequencies observed in first order theory[9] still persist but $ImG(q,\omega)$ obtained here has a high frequency tail. The results for damping coefficient of long wavelength plasmons were reported to agree with experiment. The shape of the energy loss function and the peak position did not show much improvement over the first order theory. This theory required the knowledge of the equilibrium two particle function for which they used ansatze that satisfied the exact requirement,

$$\frac{1}{N}\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = S(\underset{\sim}{q}) - 1 \,. \qquad (2.3.7)$$

In a series of papers, Utsumi and Ichimaru[47] have studied the effect of a dynamic local field on the static and dynamic properties of the electron system. They started with the equation

of motion for one particle distribution function and projected in onto a model equation. The three characteristic functions in the model equation were then determined by comparing with the small ω expansion of the response function and from the frequency moment sum rules.

The experimentally observed structure for the energy loss function for high momentum transfers was reproduced by Mukhopadhyay et al.[48] who included the life time effects of the single particle state but their theory violated the continuity equation. A similar approach followed by Awa et al.[49] also exhibited the double peak structure and suffered from the same drawback (i.e. violation of the continuity equation because, in reality, the approximation of Awa et al. is exactly identical with Mukhopadhyay et al.[48]). The origin of the double peak structure via these life-time effects has been recently examined by Niklasson et al.[50]. Green et al.[51] who included more sophisticated many body effects into their approach using the short range interaction theory suggested earlier by Lowy and Brown[52], also obtained $S(q,\omega)$ that had a double peak structure but their treatment does not show precisely the origin of this double peak.

The dynamic properties of the system have also been investigated using an entirely different approach, viz., the memory function formalism proposed by Mori[53,54]. Theories in this category include Jindal et al.[55], Mukhopadhyay and

Sjolander[56], De Raedt and De Raedt[57] and Yoshida et al.[58] The Mori approach takes account of the high frequency results like the frequency moment sum rules, i.e., these are incorporated into the theory. The static quantities however are required as inputs and cannot be determined from the theory. The introduction of the life times of particles and holes in this case by Jindal et al.[55], shifts the broad energy loss peak to lower energies (this observation is consistent with experiments) without showing a double peak structure. Mukhopadhyay and Sjolander[56] have tried various, simple approximations for the memory function and also included the life-time effects. The $S(q,\omega)$ calculated in these approximations differ from each other and also from the experimental result thus suggesting a deeper investigation of this point. None of the above theories have been able to explain the double peak structure of $S(q,\omega)$. However, recently, Sharma et al.[59] have calculated the plasmon damping coefficient for $r_s \to 0$ starting from the Mori formulation.

A conclusive fact that emerges from this discussion is that, to observe the damping of long wavelength plasmons and to explain the experimental results for the energy loss function at finite momentum transfers, it is essential to include the dynamics of the exchange-correlation hole into the theory. In a mean field approach, these effects would be included in the local field correction giving rise to a complex and frequency dependent local field correction $\tilde{G}(q,\omega)$.

2.4 DESCRIPTION AND OBJECTIVES OF THE PRESENT APPROACH

Realising the need for developing a frequency dependent local field, we have followed the equation of motion approach and proposed a theory for the dynamic local field. We truncate the hierarchy of coupled equations at the equation of motion for the one particle function by decoupling the two particle function occurring therein, via the function $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$, i.e.,

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t) \cong f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}',t) \cdot \frac{1}{m^2} C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$$

This method of decoupling is really appropriate and useful for classical liquids[5]. Substituting this form for $f^{(2)}$ in the equation of motion for $f^{(1)}$ we can obtain an expression for the induced density $\bar{n}(\underset{\sim}{q},\omega)$ of the system in terms of the free particle response function $\chi^{ro}(\underset{\sim}{q},\omega)$, the equilibrium value of $C^{(2)eq}$ (a function of the static structure factor) and $\bar{C}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$. To obtain an expression for $\chi(\underset{\sim}{q},\omega)$ or $\epsilon(\underset{\sim}{q},\omega)$, we therefore need approximate $\bar{C}^{(2)}$ or the irreducible density-density correlation function $\bar{D}^{(2)}$. The study and investigation of the results of using different approximations for this correlation function forms the major part of this work. We make approximations for $\bar{C}^{(2)}$ or $\bar{D}^{(2)}$ that lead to a frequency dependent local field correction.

The first approximation that we study is based on an ad-hoc approximation suggested by SSTL[6], for the vertex function appearing in an integral equation for the time ordered function. SSTL had used a similar approximation but neglected the dynamic screening to get only a static local field. We study the

40

A quantity that is unknown in most calculations is $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$. Ansätze satisfying certain requirements have to be used in the absence of an exact expression. Working within the equation of motion approach and the random phase approximation we have obtained such an expression for the two particle distribution function. Numerical calculation using this new form has not been possible due to the large amount of computation required. However, we show that this expression is compatible with RPA and gives the appropriate static structure factor. We also find that our derived form for $f^{(2)eq}$ is very different from the ansätze used for it so far, although at present we are unable to judge its numerical effect on the quantities calculated using ansatze[6].

CHAPTER 3

PRESENT THEORY FOR A COMPLEX FREQUENCY DEPENDENT LOCAL FIELD CORRECTION

In this chapter we discuss in detail our approximations and the theory developed to obtain a complex frequency dependent local field correction for an homogeneous electron system. As discussed in the earlier chapter, this complex nature and frequency dependence is essential to include the dissipative and dynamic effects of electron correlations in this electron gas. The sectionwise breakup of this chapter is as follows.

Section (3.1) gives the basic approximation made and expression for $\bar{n}(\underset{\sim}{q},w)$ obtained therefrom. The results obtained by various workers using different approaches can be obtained by making suitable approximations in our theory. In Section (3.1) itself we illustrate this aspect by obtaining the results of some earlier mean field theories. In Section (3.2) we discuss the first approximation for $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ (defined in equation (2.1.27)) which is along the same lines as the ad-hoc approximation made earlier by SSTL[6]. Calculations carried out and results obtained for the damping of long wavelength plasmons and for $G(q,\omega)$ at finite q and ω are discussed in Section (3.3). We conclude this chapter by a discussion in Section (3.4) of the advantages and drawbacks of the present approximation.

3.1 THEORETICAL FORMULATION OF THE THEORY

We have followed the equation of motion approach in our theory. We start with the equation of motion for a one particle Wigner distribution function (equation (2.1.17b)). In the Fourier space, the Hamiltonian for the electron system in the presence of an external potential is given by, (see Appendix II, equation (A.2.1)),

$$\hat{H} = \frac{\hbar^2}{2m} \sum_{\underset{\sim}{k}_1 \sigma_1} k_1^2 \, a^{\dagger}_{\underset{\sim}{k}_1 \sigma_1} a_{\underset{\sim}{k}_1 \sigma_1} + \frac{1}{V} \sum_{\underset{\sim}{q}'} \phi_{ext}(-\underset{\sim}{q}', t) \sum_{\underset{\sim}{k}_1 \sigma_1} a^{\dagger}_{\underset{\sim}{k}_1 - \underset{\sim}{q}'/2 \sigma_1} a_{\underset{\sim}{k}_1 + \underset{\sim}{q}'/2 \sigma_1}$$

$$+ \frac{1}{2V} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}') \sum_{\underset{\sim}{k}_1 \sigma_1 \, \underset{\sim}{k}_2 \sigma_2} a^{\dagger}_{\underset{\sim}{k}_1 - \underset{\sim}{q}'/2 \sigma_1} a^{\dagger}_{\underset{\sim}{k}_2 + \underset{\sim}{q}'/2 \sigma_2} a_{\underset{\sim}{k}_2 - \underset{\sim}{q}'/2 \sigma_2} a_{\underset{\sim}{k}_1 + \underset{\sim}{q}'/2 \sigma_1} , \quad (3.1.1)$$

where $\phi_{ext}(\underset{\sim}{q}, t)$ is the spatial Fourier transform of a time-dependent external potential ; $a_{\underset{\sim}{k}\sigma}$ and $a^{\dagger}_{\underset{\sim}{k}\sigma}$ are the amihiliation and creation operators for the electrons and $v(\underset{\sim}{q})$ represents the Coulomb potential in Fourier space, such that,

$$v(\underset{\sim}{q}) = \frac{4\pi e^2}{q^2} , \quad \text{for } q \neq 0 \quad (3.1.2a)$$

$$= 0 , \quad \text{for } q = 0 . \quad (3.1.2b)$$

Using the Hamiltonian in equation (3.1.1), the equation of motion for the one particle distribution function in Fourier space is given by,

$$i\hbar \frac{\partial}{\partial t} f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) = \left[f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) , H \right]_-$$

$$= \frac{\hbar^2}{2m} (\underset{\sim}{k} \cdot \underset{\sim}{q}) f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) + \frac{1}{V} \sum_{\underset{\sim}{q}'} \phi_{ext}(\underset{\sim}{q}', t) \left\{ f^{(1)}_{\underset{\sim}{k} - \underset{\sim}{q}'/2 \sigma}(\underset{\sim}{q} - \underset{\sim}{q}', t) - f^{(1)}_{\underset{\sim}{k} + \underset{\sim}{q}'/2 \sigma}(\underset{\sim}{q} - \underset{\sim}{q}', t) \right\}$$

$$+ \frac{1}{V} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}') \sum_{\underset{\sim}{k}_1 \sigma_1} \left\{ f^{2}_{\underset{\sim}{k} - \underset{\sim}{q}'/2 \sigma \, \underset{\sim}{k}_1 \sigma_1}(\underset{\sim}{q} - \underset{\sim}{q}', \underset{\sim}{q}', t) - f^{2}_{\underset{\sim}{k} + \underset{\sim}{q}'/2 \sigma \, \underset{\sim}{k}_1 \sigma_1}(\underset{\sim}{q} - \underset{\sim}{q}', \underset{\sim}{q}', t) \right\} . \quad (3.1.3)$$

We express f^2 in terms of irreducible distribution function $f^{(2)}$ (see equation (2.1.24)),

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t) = f^{2}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t) - f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t).$$

We then write the distribution functions as sums of their equilibrium values and deviations from equilibrium and retain terms to linear order in ϕ_{ext}. Finally, taking the temporal Fourier transform we get the equation of motion for $\bar{f}^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)$ to be

$$\left[\hbar\omega - \frac{\hbar^2}{m}\,\underset{\sim}{k}\cdot\underset{\sim}{q}\right]\bar{f}^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)$$

$$= (n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\,\frac{1}{V}\left(\phi_{ext}(\underset{\sim}{q},\omega) + v(\underset{\sim}{q})\,\bar{n}(\underset{\sim}{q},\omega)\right)$$

$$+\frac{1}{V}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\sum_{\underset{\sim}{k}_1\sigma_1}\left\{\bar{f}^{(2)}_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega) - \bar{f}^{(2)}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\right\}. \qquad (3.1.4)$$

In this equation for $f^{(1)}$, appears the two particle distribution function $f^{(2)}$. The equation of motion for $f^{(2)}$ would simila-rly contain the three particle function and so on. We truncate the series by making an approximation for $f^{(2)}$ in equation (3.1.4). As discussed in Section (2.4) of the previous chapter, we decouple $f^{(2)}$ into the one particle functions via the function $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ (defined in equation (2.1.27)) as given by the expression below.

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t) \cong f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}',t)\,\frac{1}{n^2}\,C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t) - \qquad (3.1.5)$$

Here n is the constant density of electrons in the metal. In Fourier space, we can then write,

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t) \cong \frac{1}{N^2}\sum_{\underset{\sim}{q}_1,\underset{\sim}{q}_2} f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}'-\underset{\sim}{q}_2,t)\, C^{(2)}(\underset{\sim}{q}_1,\underset{\sim}{q}_2,t) \tag{3.1.6}$$

This approximation preserves the continuity equation, which in the Fourier space reads,

$$i\hbar\frac{\partial}{\partial t}\sum_{\underset{\sim}{k}\sigma} f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \sum_{\underset{\sim}{k}\sigma}\left(\frac{\hbar^2}{m}\right)(\underset{\sim}{k}\cdot\underset{\sim}{q})\, f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t).$$

This can be easily verified by substituting (3.1.6) in (3.1.3) and then summing over $\underset{\sim}{k}\sigma$.

The correlation function $C^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t)$ is related to the irreducible density-density correlation function $D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t)$ as, (equation (2.1.27)),

$$D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t) = C^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t) + \langle\hat{\rho}(\underset{\sim}{q}+\underset{\sim}{q}';t)\rangle, \tag{3.1.7}$$

where $\hat{\rho}(\underset{\sim}{q},t)$ is the density operator defined earlier in equation (2.1.19b). The equilibrium value of the function $C^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',t)$ is given by, (equation (2.1.32d)),

$$C^{(2)eq}(\underset{\sim}{q},\underset{\sim}{q}') = N\delta_{\underset{\sim}{q}+\underset{\sim}{q}',0}\{S(\underset{\sim}{q})-1\}. \tag{3.1.8}$$

Substituting the expression from (3.1.6) for $f^{(2)}$ in the equation of motion for $\bar{f}^{(1)}$ and again retaining terms to linear order in ϕ_{ext} we have,

$$\begin{aligned}\bar{n}(\underset{\sim}{q},\omega) = {} & \{\phi_{ext}(\underset{\sim}{q},\omega) + v(\underset{\sim}{q})\,\bar{n}(\underset{\sim}{q},\omega)\}\,\chi^{T0}(\underset{\sim}{q},\omega) \\ & + \bar{n}(q,\omega)\cdot\frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}\,\chi^{T0}(\underset{\sim}{q},\underset{\sim}{q}',\omega) \\ & + \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\bar{C}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\cdot\chi^{T0}(\underset{\sim}{q},\underset{\sim}{q}',\omega).\end{aligned} \tag{3.1.9}$$

In the above equation,

$$\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \frac{1}{\hbar V}\sum_{\underset{\sim}{k}\sigma}\frac{n_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}}{\omega + i\delta - (\hbar/m)(\underset{\sim}{k}\cdot\underset{\sim}{q})}\,, \qquad (3.1.10)$$

and $\chi^{o}(\underset{\sim}{q},\omega) = \chi^{ro}(\underset{\sim}{q},\underset{\sim}{q},\omega)$ is the retarded density-density response function for the free particle or the non-interacting system (defined earlier in equation (2.3.2)).

Thus we have obtained an expression for $\bar{n}(\underset{\sim}{q},\omega)$, using which we get $\chi^{r}(\underset{\sim}{q},\omega)$ by making suitable approximations for $C^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ in equation (3.1.9). We now show how we can arrive at the results obtained by some of the earlier mean field theories from equation (3.1.9) by making suitable approximations for $\bar{C}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$.

If in equation (3.1.9), we neglect both, the second and third terms in the right hand side of the equation i.e., neglect $C^{(2)}$ and hence two particle function $\bar{f}^{(2)}$ altogether, we obtain,

$$\bar{n}(\underset{\sim}{q},\omega) = \{\phi_{ext}(\underset{\sim}{q},\omega) + v(\underset{\sim}{q})\bar{n}(\underset{\sim}{q},\omega)\}\,\chi^{ro}(\underset{\sim}{q},\omega).$$

Using equation (2.1.7), which defines $\chi^{r}(\underset{\sim}{q},\omega)$, we obtain,

$$\chi^{r}(\underset{\sim}{q},\omega) = \frac{\chi^{ro}(\underset{\sim}{q},\omega)}{1 - v(\underset{\sim}{q})\chi^{ro}(\underset{\sim}{q},\omega)}\,, \qquad (3.1.11)$$

which is the well-known time-dependent Hartree approximation[2] (commonly known as the random phase approximation).

As the next approximation we neglect only the third term on the right hand side i.e. approximate $C^{(2)}$ by its

equilibrium value. In this case then we have,

$$\chi^{r}(\underset{\sim}{q},\omega) = \frac{\chi^{r0}(\underset{\sim}{q},\omega)}{1-v(q)\{1-G(\underset{\sim}{q},\omega)\}\chi^{r0}(\underset{\sim}{q},\omega)} , \qquad (3.1.12)$$

where $G(\underset{\sim}{q},\omega)$ is the so called local field connection that is given by,

$$G(\underset{\sim}{q},\omega) = -\frac{1}{v(q)\chi^{r0}(\underset{\sim}{q},\omega)} \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\{s(\underset{\sim}{q}-\underset{\sim}{q}')-1\}\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega) . \qquad (3.1.13)$$

This is the result obtained by Hasegawa and Shimizu[46], who followed a fully quantum mechanical approach starting with the equation of motion for a one particle Wigner distribution function and made an approximation for $f^{(2)}_{\underset{\sim}{k}o\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t)$ as suggested by Singwi et al.[31] Singwi et al. (STLS)[31] decoupled the two particle function via the equilibrium pair correlation function as follows :

$$f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t) = f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}',t)\{g(\underset{\sim}{r}-\underset{\sim}{r}')-1\} . \qquad (3.1.14)$$

Here we note that if we replace $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ by its equilibrium value in equation (3.1.5) ($C^{(2)eq}$ has been defined in equation (2.1.32b)), the present approximation for $f^{(2)}$ reduces to the one used by Singwi et al.[31] in their calculations.

In the classical limit i.e., for $\hbar \to 0$, $\chi^{r0}(q,q',\omega)$ is given by,

$$\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega) \xrightarrow{\hbar\to 0} \frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q^2}\chi^{r0}(\underset{\sim}{q},\omega) . \qquad (3.1.15)$$

Using this limiting value, we find that in the classical limit, equation (3.1.12) reduces to

$$\chi^{r}(\underset{\sim}{q},\omega) = \frac{\chi^{r0}(\underset{\sim}{q},\omega)}{1-v(\underset{\sim}{q})\{1-G(\underset{\sim}{q})\}\chi^{r0}(\underset{\sim}{q},\omega)} , \qquad (3.1.16)$$

where $G(\underset{\sim}{q})$ which is the static local field factor is given by,

$$G(\underset{\sim}{q}) = -\frac{1}{nV}\sum_{\underset{\sim}{q}'}\frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}. \qquad (3.1.17)$$

This is the result obtained by Singwi et al.[31] whose approximation for decoupling of $f^{(2)}$ in the equation of motion for $\bar{f}^{(1)}$ was rather intuitive than systematic.

Hence, we see that in the present formalism, we can obtain the earlier results (obtained using different approaches), in a more simple and methodical manner.

3.2 TIME DEPENDENT LOCAL FIELD - FIRST APPROXIMATION

First of all we note the following identity,

$$\begin{aligned}
&\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\bar{C}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\\
&= \frac{1}{2}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\{\bar{C}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)+\bar{C}^{(2)}(\underset{\sim}{q}+\underset{\sim}{q}',-\underset{\sim}{q}',\omega)\chi^{ro}(\underset{\sim}{q},-\underset{\sim}{q}',\omega)\},\\
&= \frac{1}{2}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\{\bar{C}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)-\bar{C}^{(2)}(\underset{\sim}{q}+\underset{\sim}{q}',-\underset{\sim}{q}',\omega)\}\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega),\\
&= \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega). \qquad (3.2.1)
\end{aligned}$$

where we have made use of the fact that $\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ is an odd function of $\underset{\sim}{q}'$ and the relation between $C^{(2)}$ and $D^{(2)}$ Thus an approximation for $\bar{D}^{(2)}$, the irreducible density-density correlation function can be used instead of $\bar{C}^{(2)}$ in equation (3.1.9) to get $\chi^{r}(\underset{\sim}{q},\omega)$.

The equal time correlation function $D^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ is related to the time ordered function $\pi(\underset{\sim}{r},t;\underset{\sim}{r}',t)$, as,

$$D^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t) = \lim_{t' \to t} i\hbar\, \pi(\underset{\sim}{r}, t; \underset{\sim}{r}', t') \qquad (3.2.2a)$$

$$= \lim_{t' \to t} \left[\langle T\{\hat{\rho}(\underset{\sim}{r}, t)\, \hat{\rho}(\underset{\sim}{r}', t')\} \rangle - \langle \hat{\rho}(\underset{\sim}{r}, t) \rangle \langle \hat{\rho}(\underset{\sim}{r}', t') \rangle \right] \qquad (3.2.2b)$$

We obtain an expression for $D^{(2)}$ (in the presence of an external field ϕ_{ext}) using an approximate solution of an integral equation for π following the method suggested by Singwi et al. (SSTL)[6]. We start with an integral equation for the non-equilibrium function π,

$$\pi(1,1') = \pi_{sc}(1,1') + \int \pi_{sc}(1,2)\, v(2,3)\, \pi(3,1')\, d(2)\, d(3) , \qquad (3.2.3)$$

where, π_{sc} is the screened correlation function ; $1 \equiv (r, t_1)$, $2 \equiv (r_2, t_2)$ etc., and v as before is the Coulomb interaction. Again writing π as a sum of its equilibrium value and its deviation from equilibrium i.e., as,

$$\pi(1,1') = \pi^{eq}(1,1') + \bar{\pi}(1,1') , \qquad (3.2.4)$$

we can rewrite equation (3.2.3). Suppressing all coordinates for brevity and using the matrix notation we have,

$$\pi^{eq} + \bar{\pi} = \pi^{eq}_{sc} + \bar{\pi}_{sc} + (\pi^{eq}_{sc} + \bar{\pi}_{sc}) v (\pi^{eq} + \bar{\pi}) ,$$

$$\cong \pi^{eq}_{sc} + \bar{\pi}_{sc} + \pi^{eq}_{sc} v\, \pi^{eq} + \pi^{eq}_{sc} v\, \bar{\pi} + \bar{\pi}_{sc} v\, \pi^{eq} . \qquad (3.2.5)$$

Here again since the external potential ϕ_{ext} is weak, we have retained terms only to linear order in deviations from equilibrium. π^{eq} satisfies a similar integral equation as π in equation (3.2.3). Making use of this we have,

$$\bar{\pi} \cong \bar{\pi}_{sc} + \bar{\pi}_{sc} v\, \pi^{eq} + \pi^{eq}_{sc} v\, \bar{\pi} .$$

This can be reduced to,

$$\bar{\pi} = \epsilon^{c-1} \bar{\pi}_{sc} (\pi^{eq}_{sc})^{-1} \pi^{eq}, \qquad (3.2.6)$$

where we have used the definition for the causal dielectric function ϵ^c, i.e.,

$$\epsilon^c = 1 - \pi^{eq}_{sc} v \qquad (3.2.7)$$

Now defining a vertex function $\bar{h}(1, 1')$ as,

$$\bar{h}(1,1') = \int d(2)\, \bar{\pi}_{sc}(1,2)\, \pi^{eq\,-1}_{sc}(2,1'), \qquad (3.2.8)$$

the integral equation for $\pi(1, 1')$ can be written as,

$$\pi(1,1') = \pi^{eq}(1,1') + \int d(2)\, d(3)\, \epsilon^{c-1}(1,2)\, \bar{h}(2,3)\, \pi^{eq}(3,1'). \qquad (3.2.9)$$

We now make the ad-hoc approximation for this vertex function $\bar{h}$ as suggested by SSTL[6]. Assuming that the correlation functions are shortranged in space and time and hence depend on the local density alone, we write,

$$\bar{h}(\underset{\sim}{r}, t; \underset{\sim}{r}', t') = \delta(\underset{\sim}{r} - \underset{\sim}{r}')\, \delta(t - t')\, \frac{\bar{n}(\underset{\sim}{r}, t)}{n}. \qquad (3.2.10)$$

This form ensures a static limit, for the resultant response function, equal to the static results obtained earlier by STLS[31]. Substituting this expression for $\bar{h}(\underset{\sim}{r}, t; \underset{\sim}{r}', t')$ in equation (3.2.9), the integral equation for π within this approximation is given by,

$$\pi(\underset{\sim}{r}, t; \underset{\sim}{r}', t') = \pi^{eq}(\underset{\sim}{r}, t; \underset{\sim}{r}', t') + \frac{1}{n} \int d^3 r_1\, dt_1\, \epsilon^{c-1}(\underset{\sim}{r}, t; \underset{\sim}{r}_1, t_1)\, \pi^{eq}(\underset{\sim}{r}_1, t_1; \underset{\sim}{r}', t')\, \bar{n}(\underset{\sim}{r}_1, t_1).$$

The equilibrium time-ordered correlation function is nothing but the causal density-density response function $\chi^c(\underset{\sim}{r}, t; \underset{\sim}{r}', t')$.

Thus we have, from equation (3.2.2a),

$$\bar{D}^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t) = \frac{i\hbar}{n}\int d\underset{\sim}{r}''\,dt''\;\epsilon^{c-1}(\underset{\sim}{r}-\underset{\sim}{r}'',t-t')\,\chi^{c}(\underset{\sim}{r}''-\underset{\sim}{r}',t''-t') \cdot \bar{n}(\underset{\sim}{r}'',t'), \qquad (3.2.11)$$

$$= \frac{1}{V^2}\sum_{\underset{\sim}{q}_1,\underset{\sim}{q}_2} e^{i\underset{\sim}{q}_1\cdot\underset{\sim}{r}+i\underset{\sim}{q}_2\cdot\underset{\sim}{r}'}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,e^{-i\omega t} \cdot\left[\frac{i\hbar}{n}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\;\frac{\chi^{c}(\underset{\sim}{q}_2,\omega_1-\omega)}{\epsilon^{c}(\underset{\sim}{q}_1,\omega_1)}\;\bar{n}(\underset{\sim}{q}_1+\underset{\sim}{q}_2,\omega)\right].$$

Using this, the Fourier transform used in equation (3.1.9) is given by,

$$\bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega) = \frac{i\hbar}{n}\int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\;\frac{\chi^{c}(\underset{\sim}{q}',\omega_1-\omega)}{\epsilon^{c}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)}\cdot\bar{n}(\underset{\sim}{q},\omega). \qquad (3.2.12)$$

Within the random phase approximation (to maintain consistency), we can write,

$$\epsilon^{c-1}(\underset{\sim}{q},\omega) = 1 + v(\underset{\sim}{q})\chi^{c}(\underset{\sim}{q},\omega). \qquad (3.2.13)$$

Substituting in equation (3.2.12) we find that the expression for $\bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)$ splits into two parts as given below,

$$\bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega) = \bar{n}(\underset{\sim}{q},\omega)\left[\frac{i\hbar}{n}\int\frac{d\omega_1}{2\pi}\;\chi^{c}(\underset{\sim}{q}',\omega_1-\omega) + \frac{i\hbar}{n}v(\underset{\sim}{q}-\underset{\sim}{q}')\int\frac{d\omega_1}{2\pi}\;\chi^{c}(\underset{\sim}{q}',\omega_1-\omega)\,\chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)\right],$$

$$= \bar{n}(\underset{\sim}{q},\omega)\left[S(\underset{\sim}{q}') + v(\underset{\sim}{q}-\underset{\sim}{q}')\frac{i\hbar}{n}\int\frac{d\omega_1}{2\pi}\;\chi^{c}(\underset{\sim}{q}',\omega_1-\omega)\,\chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)\right]. \qquad (3.2.14)$$

Substituting this form for $\bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)$ in the third term on the right hand side of equation (3.1.9) we have,

$$\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\, \bar{c}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}', \omega)\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega)$$

$$= \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\, \bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}', \omega)\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \quad ,$$

$$= \bar{n}(\underset{\sim}{q}, \omega) \cdot \frac{1}{nV} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}') \Big[S(\underset{\sim}{q}')\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega)$$

$$+ v(\underset{\sim}{q}-\underset{\sim}{q}') \cdot \frac{i\hbar}{n} \int \frac{d\omega_1}{2\pi}\, \chi^{c}(\underset{\sim}{q}', \omega_1-\omega)\, \chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}', \omega_1)\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \Big] \quad ,$$

$$= \bar{n}(\underset{\sim}{q}, \omega) \cdot \frac{1}{nV} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\, v(\underset{\sim}{q}-\underset{\sim}{q}') \cdot \frac{i\hbar}{n} \int \frac{d\omega_1}{2\pi}\, \chi^{c}(\underset{\sim}{q}', \omega_1-\omega)\, \chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}', \omega_1)\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \, .$$

The first term in the third line of the above equations vanishes because of the fact that $S(\underset{\sim}{q}')\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega)$ is an odd function of $\underset{\sim}{q}'$. Substituting in equation (3.1.9), we have,

$$\bar{n}(\underset{\sim}{q}, \omega) = \{ \phi_{ext}(\underset{\sim}{q}, \omega) + v(\underset{\sim}{q})\, \bar{n}(\underset{\sim}{q}, \omega) \}\, \chi^{ro}(\underset{\sim}{q}, \omega)$$

$$+ \bar{n}(\underset{\sim}{q}, \omega) \cdot \frac{1}{nV} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}') \Big[\{ S(\underset{\sim}{q}-\underset{\sim}{q}') - 1 \}$$

$$+ v(\underset{\sim}{q}-\underset{\sim}{q}') \cdot \frac{i\hbar}{n} \int \frac{d\omega_1}{2\pi}\, \chi^{c}(\underset{\sim}{q}', \omega_1-\omega)\, \chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}', \omega_1) \Big]\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \, . \qquad (3.2.15)$$

Then from equation (2.1.7) we have,

$$\chi^{r}(\underset{\sim}{q}, \omega) = \frac{\chi^{ro}(\underset{\sim}{q}, \omega)}{1 - v(\underset{\sim}{q}) \{ 1 - G(\underset{\sim}{q}, \omega) \}\, \chi^{ro}(\underset{\sim}{q}, \omega)} \quad , \qquad (3.2.16)$$

where, the local field correction $G(\underset{\sim}{q}, \omega)$ is given by,

$$G(\underset{\sim}{q}, \omega) = - \frac{1}{v(\underset{\sim}{q})\, \chi^{ro}(\underset{\sim}{q}, \omega)} \cdot \frac{1}{nV} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}') \Big[\{ S(\underset{\sim}{q}-\underset{\sim}{q}') - 1 \}$$

$$+ v(\underset{\sim}{q}-\underset{\sim}{q}') \frac{i\hbar}{n} \int \frac{d\omega_1}{2\pi}\, \chi^{c}(\underset{\sim}{q}', \omega_1-\omega)\, \chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}', \omega_1) \Big]\, \chi^{ro}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \, .$$

Since $\chi^c(\underset{\sim}{q},\omega)$ is an even function of q and ω, we can rewrite above equation to obtain,

$$G(\underset{\sim}{q},\omega) = -\frac{1}{v(q)\,\chi^{r0}(\underset{\sim}{q},\omega)} \cdot \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\left[\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}\right.$$

$$\left. + v(\underset{\sim}{q}-\underset{\sim}{q}')\,\frac{i\hbar}{n}\int\frac{d\omega_1}{2\pi}\,\chi^c(\underset{\sim}{q}',\omega_1)\,\chi^c(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1)\right]\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega). \quad (3.2.17)$$

When we use Hasegawa and Shimizu's approach and use this approximation suggested by SSTL[6] for decoupling of $\bar{f}^{(2)}$, we get a similar expression for $G(\underset{\sim}{q},w)$. In this case,

$$G(\underset{\sim}{q},\omega) = -\frac{1}{v(q)\,\chi^{r0}(\underset{\sim}{q},\omega)} \cdot \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\left[\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}\right.$$

$$\left. + v(\underset{\sim}{q}')\,\frac{i\hbar}{n}\int\frac{d\omega_1}{2\pi}\,\chi^c(\underset{\sim}{q}',\omega_1)\,\chi^c(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1)\right]\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega). \quad (3.2.18)$$

We are not able to reproduce the result exactly mainly becuase of the ad-hoc approximation used for $\bar{h}$. By definition, the function $D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ is symmetric with respect to exchange of variables $\underset{\sim}{q}$ and $\underset{\sim}{q}'$. In this approximation we see that this does not hold (see equation (3.2.14)). As we shall see later, a better and more realistic approximation gives a symmetric $D^{(2)}$ and in that case we find that other results are reproduced.

In the classical, i.e. $\hbar \to 0$ limit, using equation (3.1.15) and neglecting the frequency dependence of $\epsilon(q,\omega)$ in the denominator we have,

$$G(\underset{\sim}{q}) = -\frac{1}{nV}\sum_{\underset{\sim}{q}'}\frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}\cdot\frac{1}{\epsilon(\underset{\sim}{q}')}\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}. \quad (3.2.19)$$

This is the result obtained by SSTL[6]. As they neglected the frequency dependence of the dielectric function in the

denominator of $G(\underset{\sim}{q},\omega)$, they obtained a static local field $G(\underset{\sim}{q})$ in their approximation.

From the equation (3.2.17) we see that the first term, a real quantity, has the same form as the local field obtained by Hasegawa and Shimizu[46] which satisfies most of the static properties of the system. The second term is the complex, frequency dependent part which will be of interest in our present calculations. We give the details of our calculations and results in the next section.

3.3 NUMERICAL CALCULATIONS AND RESULTS

We have carried out calculations in the classical limit of the equation (3.2.18), retaining the frequency dependence of the dielectric function. The $G(\underset{\sim}{q},\omega)$ in this limit also is a complex and dynamic quantity. It can therefore be of use in studying the damping of plasmons. We have calculated the damping coefficient of long wavelength plasmons[60] which can be obtained from the imaginary part of $G(\underset{\sim}{q},\omega)$ in the $q \rightarrow 0$ limit. We have also calculated both real and imaginary parts of the local field correction $G(\underset{\sim}{q},\omega)$ for finite momentum and energy transfers. The details of these calculations are given in the two subsections here. The local field correction $G(\underset{\sim}{q},\omega)$ can be written as,

$$G(\underset{\sim}{q},\omega) = G_1(\underset{\sim}{q}) + G_2(\underset{\sim}{q},\omega) \qquad (3.3.1)$$

The second term $G_2(\underset{\sim}{q},\omega)$, a complex and frequency dependent quantity can be written in terms of the imaginary parts of

the response function, by using the spectral representations for the causal functions according to which,

$$\chi^c(\underset{\sim}{q},\omega) = -\frac{1}{\pi}\int_0^\infty d\omega' \; \mathrm{Im}\,\chi^c(\underset{\sim}{q},\omega')\left\{\frac{1}{\omega-\omega'+i\delta} - \frac{1}{\omega+\omega'-i\delta}\right\}. \tag{3.3.2}$$

Using this form for the causal functions in equation (3.2.18) we can perform the ω_1 integral as shown in Appendix III. Then using the relation between the imaginary parts of the retarded and causal functions for positive ω (equation (2.1.34b)), the imaginary part of $G_2(\underset{\sim}{q},\omega)$ can be written as,

$$\mathrm{Im}\,G_2(\underset{\sim}{q},\omega) = \frac{1}{4\pi^2 e^2 n^2}\int \frac{d^3q'}{(2\pi)^3}\,\frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}\,|\underset{\sim}{q}-\underset{\sim}{q}'|^2 \cdot \int_0^\omega d\omega_1\, Q^{r''}(\underset{\sim}{q}',\omega_1)\,Q^{r''}(|\underset{\sim}{q}-\underset{\sim}{q}'|,\omega-\omega_1). \tag{3.3.3}$$

where $Q^r(\underset{\sim}{q},\omega) = -v(\underset{\sim}{q})\,\chi^r(\underset{\sim}{q},\omega)$, is the polarisability of the system. Using reduced units where q and q' are in units of q_F, the Fermi momentum and $\hbar\omega$ and $\hbar\omega'$ in units of ϵ_F, the Fermi energy, we can rewrite equation (3.3.3) as,

$$\mathrm{Im}\,G_2(q,\omega) = \frac{q}{32\alpha r_s}\int_0^\infty dq' \int_{-1}^{+1} dt\; qq't\,q''^2 \cdot \int_0^\omega d\omega_1\, Q^{r''}(q',\omega_1)\,Q^{r''}(q'',\omega-\omega_1). \tag{3.3.4}$$

where $q''^2 = q^2 + q'^2 - 2qq't$.

In equation (3.3.4), the ω-dependence of $\mathrm{Im}G_2(\underset{\sim}{q},\omega)$ is seen to be controlled by a product of the type $Q^{r''}\,Q^{r''}$ i.e. by coupling between the various excitation modes of the system. A similar feature had been observed earlier by Sharma et al.[59] who used an entirely different approach called the Mori formalism to develop a theory mainly for investigating the damping of plasmons. In the Mori approach, a disadvantage is that the

static quantities are required as inputs to the theory and cannot be extracted from the theory itself, whereas in the present case we are able to reproduce the well accepted static results[31]. Further, this mode coupling feature present in our approach is noteworthy because to our knowledge this is for the first time, starting from an equation of motion or a generalised mean field approach, one has been able to incorporate the coupling between the excitation modes in the system.

In principle, equation (3.3.4) has to be solved self-consistently with equation (3.2.17) to obtain $ImG(q,\omega)$. The amount of computation being formidable we have replaced the Q^r in the equation for $ImG_2(\underset{\sim}{q},\omega)$ by its RPA form which can be obtained from equation (3.1.11). By using the RPA form, we ensure the coupling between the excitation modes of the interacting system.

3.3.1 Damping coefficient of long wavelength plasmons

In the small q limit, the imaginary part of $G(\underset{\sim}{q},\omega)$ is found to vary as q^2 (as expected). This $ImG(\underset{\sim}{q},\omega)$ gives the plasmon damping coefficient γ which is defined (in reduced units) as,

$$\gamma = + \frac{\omega_p}{2q^2} \operatorname{Im} G(\underset{\sim}{q}, \omega_p) , \qquad (3.3.5)$$

where ω_p is the bulk plasmon frequency. In Table (3.1) we have tabulated the contributions to damping coefficient from this coupling of excitation modes for r_s = 2,3,4 and 5.

TABLE 3.1

Contributions to r from		$r_s = 2$	$r_s = 3$	$r_s = 4$	$r_s = 5$
$Q''_{RPA}\ Q''_{RPA}$		0.0015	0.0023	0.0031	0.0037
$Q^{ro''}Q^{ro''}$	computed	0.0967			
	analytical	0.0966			
Sharma et.al.'s result		0.6797			

Contributions to damping coefficient γ calculated using equation (3.3.4) based on the expression (3.2.18) ; only magnitudes are given, since here the γ -values turn out to be negative (unphysical). The γ-values become positive (physical) if the calculation is based on the expression (3.2.17) and in this case, the magnitude increases by a constant factor of 3. Since the expressions (3.2.17) and (3.2.18) differ only in derivation one expects on average of the two results to be appropriate. In this case the γ-values become positive with magnitudes as indicated in the table above.

The contributions to $\mathrm{Im}G(\underset{\sim}{q},\omega)$ from interactions between particle-hole and plasmons and between plasmons themselves arise only for frequencies greater than the plasmon frequency ω_p. At $\omega \leq \omega_p$, the only contribution is from the $Q^{r''}_{ph}\, Q^{r''}_{ph}$ i.e., the particle hole part alone. When Q_{RPA} is replaced by the free electron polarisability Q^{ro}, there is a considerable increase in the value of γ. For this particular case of using non-interacting Q^{ro}, we have carried out analytical calculations also for $r_s = 2$. As q is small, we make a Taylor expansion of $Q''(\underset{\sim}{q}'-\underset{\sim}{q},\omega-\omega_1)$ about q' to linear order in q as,

$$Q^{ro''}(\underset{\sim}{q}-\underset{\sim}{q}',\ \omega-\omega_1) = Q^{ro''}(\underset{\sim}{q}',\omega-\omega_1) - \underset{\sim}{q}.\nabla_{q'}\, Q^{ro''}(\underset{\sim}{q}',\omega-\omega_1) \qquad (3.3.6)$$

To evaluate the integrals we have followed the method suggested by Dubois[61] (Appendix IV). In the table we have also listed for $r_s = 2$, the result obtained by Sharma et al.[59], who used Mori formalism and replaced $Q^{r''}$ by $Q^{ro''}$. The difference in the value obtained by us and that obtained by them is rather large. This is somewhat misleading because the expression obtained by Sharma et al.[59], viz.,

$$\gamma = \frac{3\pi}{640}\,\omega_p^3\,[63(1-\ln 2)] \simeq 0.285\,\omega_p^3 \qquad (3.3.7)$$

is really valid only in the $r_s \to 0$ limit. The value of γ reported in table (3.1) has been calculated for $r_s = 2$ using the above $r_s \to 0$ result. This small r_s result compares quite well with the weak coupling result ($r_s \to 0$) obtained earlier by Dubois and Kivelson[7] following perturbation theory, i.e.,

$$\gamma = \frac{3\pi}{640}\omega_p^3 [34 - 22\ln 2] \simeq 0.276\,\omega_p^3 \qquad (3.3.8)$$

We have therefore investigated the $r_s \to 0$ limit in our approximation. We use the same approximations as Sharma et al.[59] i.e., replace $Q^{r''}$ by the free particle function $Q^{ro''}$ and neglect the second term in equation (3.3.6), (i.e. the derivative of $Q''(\underset{\sim}{q}', \omega-\omega_1)$. In this case we obtain,

$$\gamma = \frac{3\pi}{640}\cdot\omega_p^3 [40(1-\ln 2)] \simeq 0.181\,\omega_p^3 \qquad (3.3.9)$$

Now the agreement with $r_s \to 0$ result of Dubois and Kivelson[7] is fairly good and that with Sharma et al.'s[59] result in the same limit is far more improved. We note here that the inclusion of the derivative term in equation (3.3.6) reduces the value of γ by about 75%. For example, in the $r_s \to 0$ limit if we take the full expansion of $Q^{ro''}(q-q', \omega-\omega_1)$, given in equation (3.3.6), we obtain,

$$\gamma = \frac{3\pi}{640}\omega_p^3 [10(1-\ln 2)] \simeq 0.045\,\omega_p^3 \qquad (3.3.9a)$$

These results for $r_s \to 0$ however are not very useful here, since for metallic densities the value of r_s lies in the range between 1.8 and 5.6. Thus we feel that the γ values calculated by us and presented in table (3.1) are more relevant for metallic densities and none of the results (3.3.7) to (3.3.9) is meaningful in this range of r_s. However, we note that the $Q^{ro''}\,Q^{ro''}$ approximation gives considerably large value of γ as compared with that for the more accurate fully interacting case, represented in the table by $Q^{r''}_{RPA}Q^{r''}_{RPA}$ The significant decrease in the magnitude of γ results from

the screening effect which is absent in the $Q^{ro''}$ $Q^{ro''}$ approximation.

3.3.2 Finite q and ω calculations

For $r_s = 2$, we have calculated the real and imaginary parts of the local field correction $G(\underset{\sim}{q},\omega)$ for various values of q and ω. In equation (3.3.4) for Im $G_2(\underset{\sim}{q},\omega)$ we replace $Q^{r''}(\underset{\sim}{q},\omega)$ by its RPA expression for both, the particle-hole as well as plasmon contributions, i.e.,

$$Q^{r''} = \left(Q^{r''}_{RPA}\right)_{ph} + \left(Q^{r''}_{RPA}\right)_{pl} .$$

Now,

$$\left(Q^{r''}_{RPA}\right)_{ph} = \left(\frac{Q^{ro}}{1+Q^{ro}}\right)'' , \qquad (3.3.10)$$

and

$$\left(Q^{r''}_{RPA}\right)_{pl} = \frac{\pi}{2}\,\omega(q)\,\delta(\omega-\omega(q))\,\theta(q_c-q) , \qquad (3.3.11)$$

where,

$$\omega(q) = \omega_p(1+\Gamma q^2) . \qquad (3.3.12)$$

Here $\Gamma = (9\pi/40\alpha r_s)$ in reduced units and q_c is the critical wavevector (see Section 2.2.4). Thus now in Im $G_2(q,\omega)$ we have contributions from Q''_{pn} Q''_{ph}, Q''_{ph} Q''_{pl} and Q''_{pl} Q''_{pl}.

To obtain the particle-hole contribution, we have evaluated the triple integral in equation (3.3.4) using numerical methods. The ω_1 and t integrals were computed together using two dimensional Simpson's method for integration involving two variables, and the q' integral was then evaluated using Trapezoidal rule. In the particle-hole-plasmon part, the ω_1 integral could be performed analytically and then the t and q'

integrals evaluated using numerical methods, e.g., Simpson's three point formula for the t-integral and the Trapezoidal rule for the q' integral. The plasmon-plasmon contribution could be evaluated analytically but it was found to give a non-zero value only for small q ($q < 1$ in reduced units).

In figures (3.1) to (3.3) we have plotted the different contributions to $\mathrm{Im}G_2(q,\omega)$ and total $\mathrm{Im}G_2(q,\omega)$ as a function of the frequency ω, for $q = 1.6$, 2.5 and 5.0 respectively. In all these figures curve 1 gives the particle-hole-plasmon contribution, curve 2 the particle-hole-particle-hole contribution and curve 3 the total $\mathrm{Im}G_2(q,\omega)$. As can be seen from the curves, in the high frequency region, the plasmon contribution vanishes completely and the particle-hole gives the only non-zero contribution. At very high ω, this part also appears to decrease to zero as $1/(A+B\omega)$.

To obtain the real part of $G_2(q,\omega)$ from the imaginary part, we have made use of the Kramer-Kronig dispersion relation which applies to G_2 :

$$\mathrm{Re}\, G_2(q,\omega) = \frac{1}{\pi} P \int_{-\infty}^{\infty} d\omega' \, \frac{\mathrm{Im}\, G_2(q,\omega')}{\omega' - \omega} \quad , \qquad (3.3.13)$$

where P denotes the principal value of the integral. In figures (3.4) to (3.6), we plot the $\mathrm{Re}G_2(q,\omega)$ as a function of ω, for $q = 1.6$, 2.5 and 5.0 respectively, again for $r_s = 2$.

It is interesting to note a special feature of $G_2'(q,\omega)$, viz., the negative peak in its value. Niklasson[8] had reported

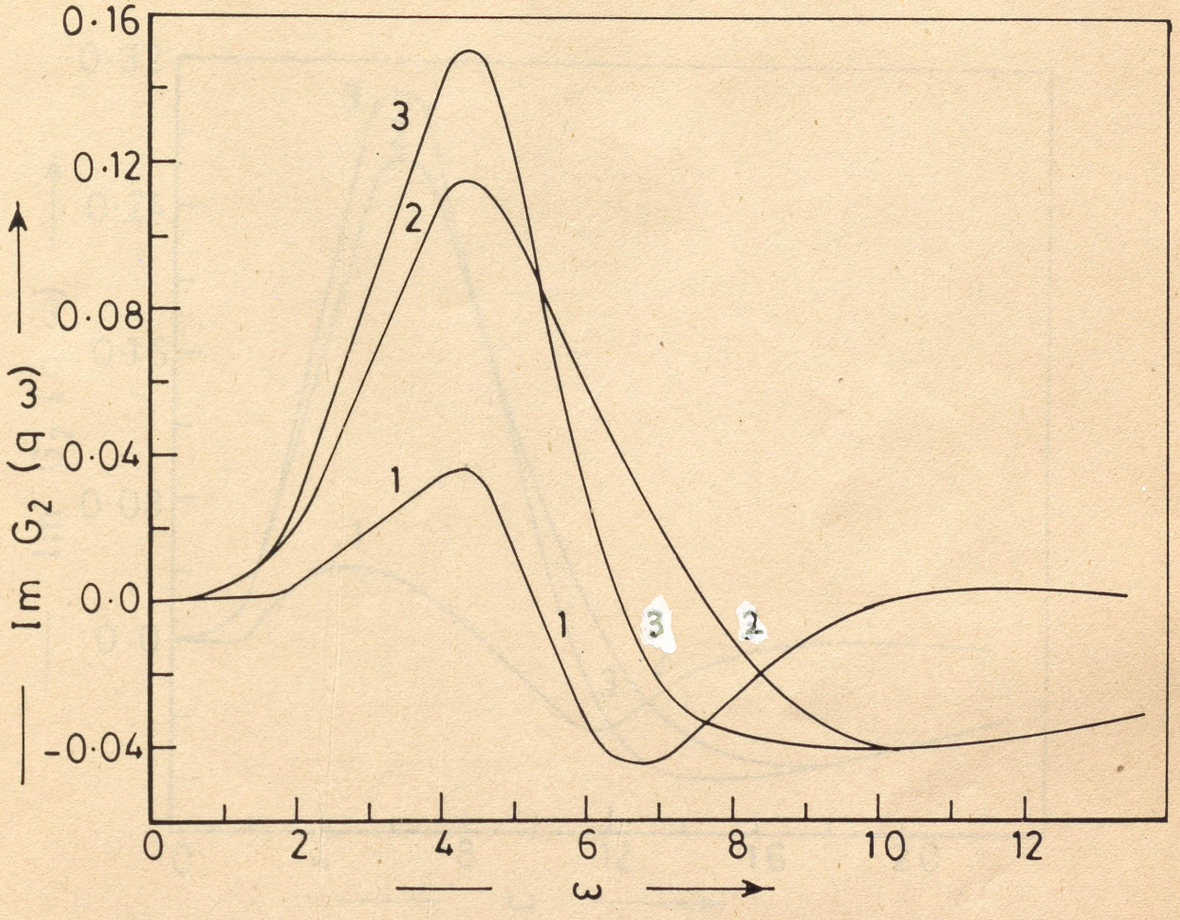


Fig. 3·1: Imaginary part of $G_2(q,\omega)$ as a function of ω for $q = 1{\cdot}6$ and $r_s = 2$.
Curve 1: particle - hole plasmon part;
Curve 2: particle - hole part;
Curve 3: total Im $G_2(q,\omega)$.

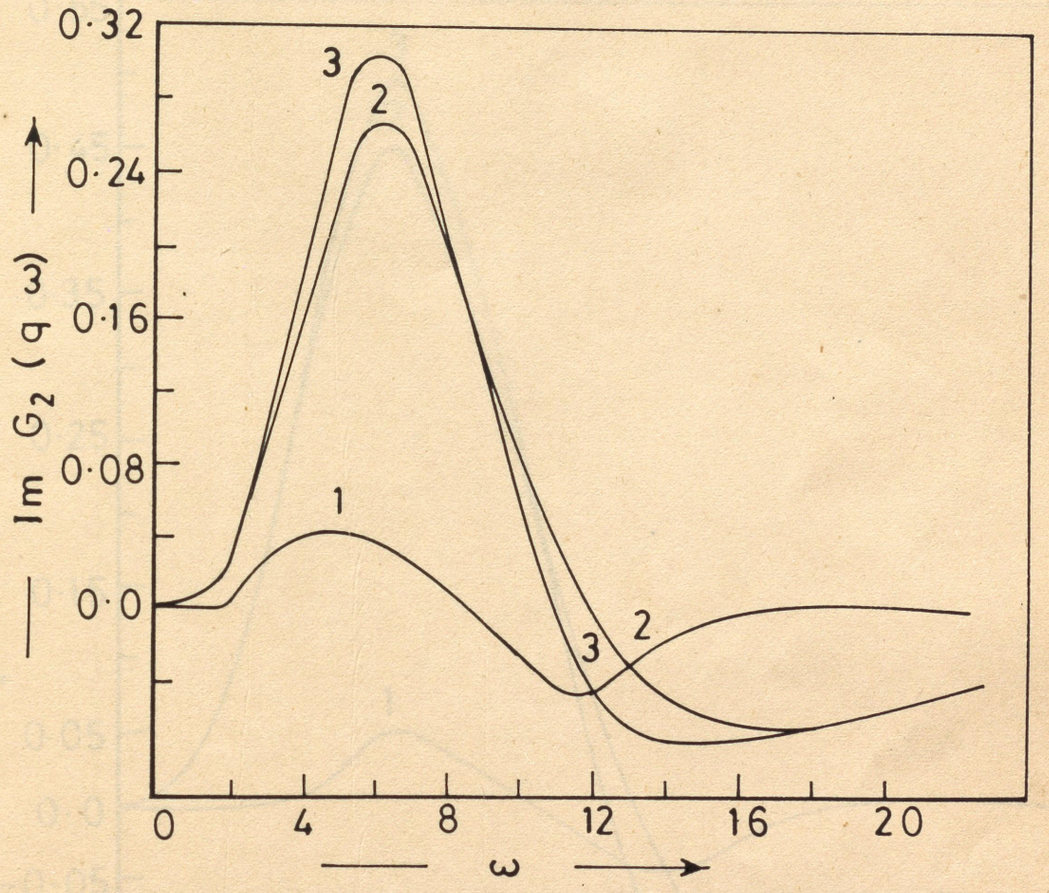


Fig. 3·2 : Imaginary part of $G_2(q,\omega)$ as a function of ω for $q = 2{\cdot}5$ and $r_s = 2$.

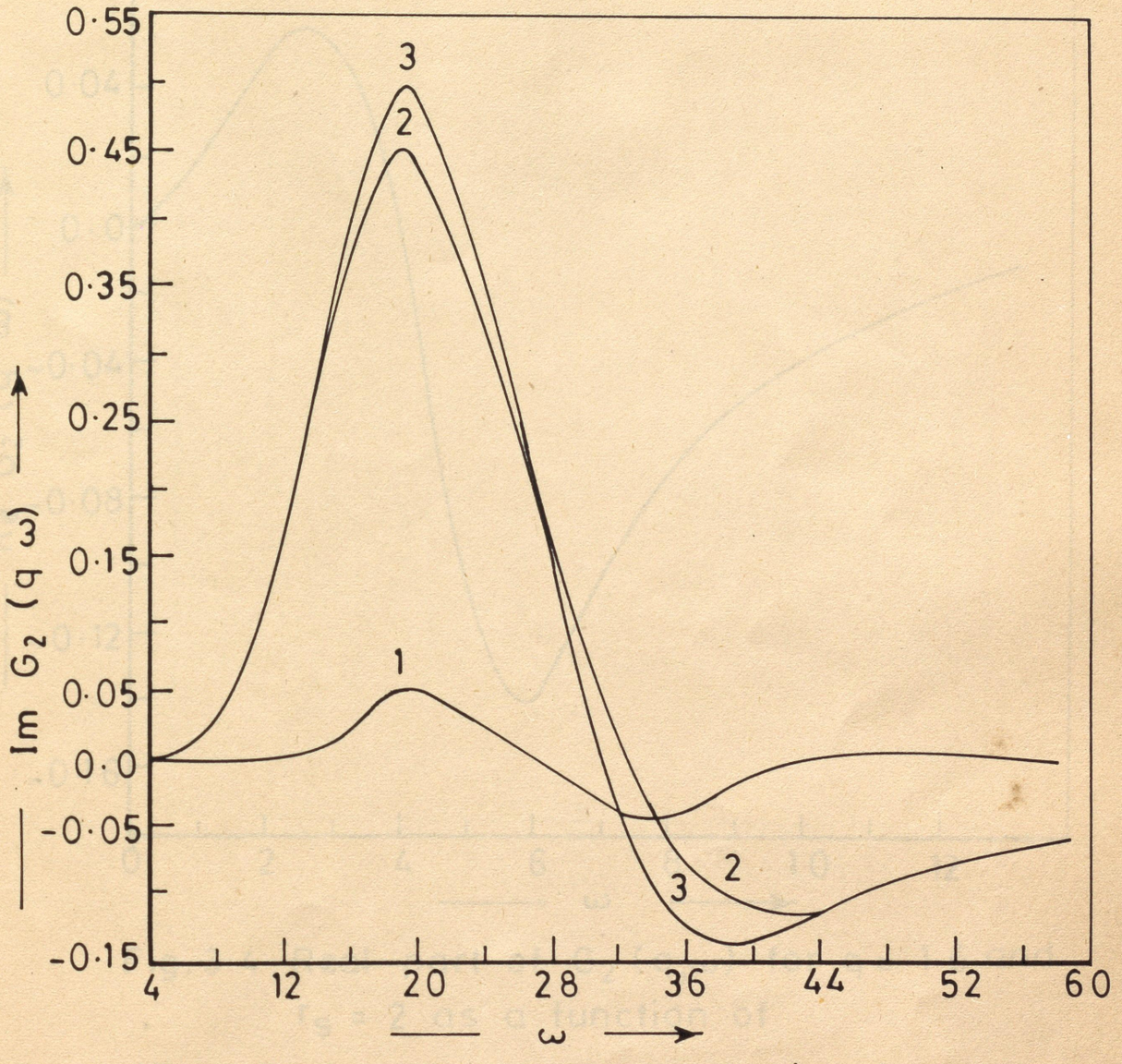


Fig. 3·3 : Imaginary part of G_2 (q,ω) as a function of ω for q = 5·0 and r_s = 2.

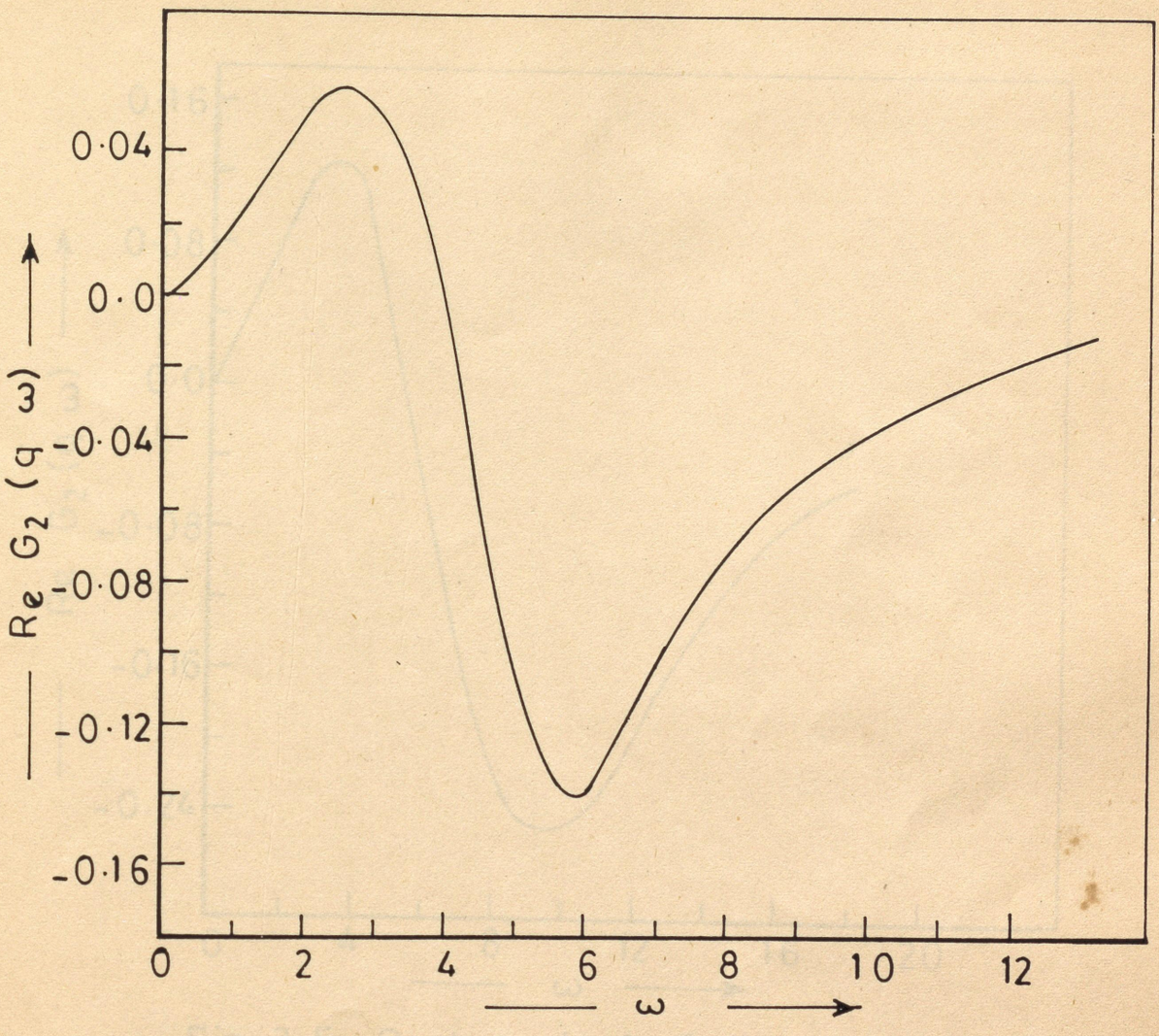


Fig. 3·4 : Real part of $G_2(q,\omega)$ for $q = 1{\cdot}6$ and $r_s = 2$ as a function of

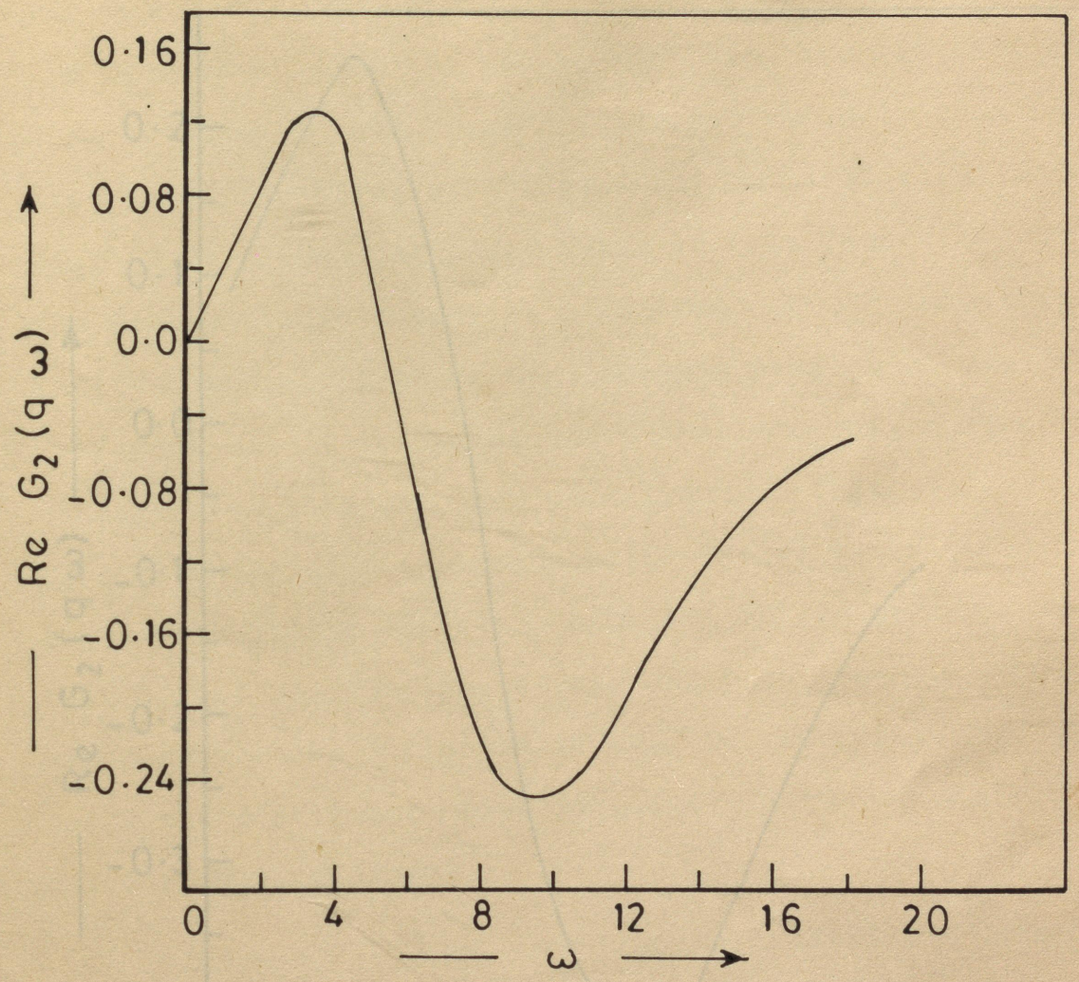


Fig. 3·5 : Real part of $G_2(q,\omega)$ for $q = 2.5$ and $r_s = 2$ as a function of ω.

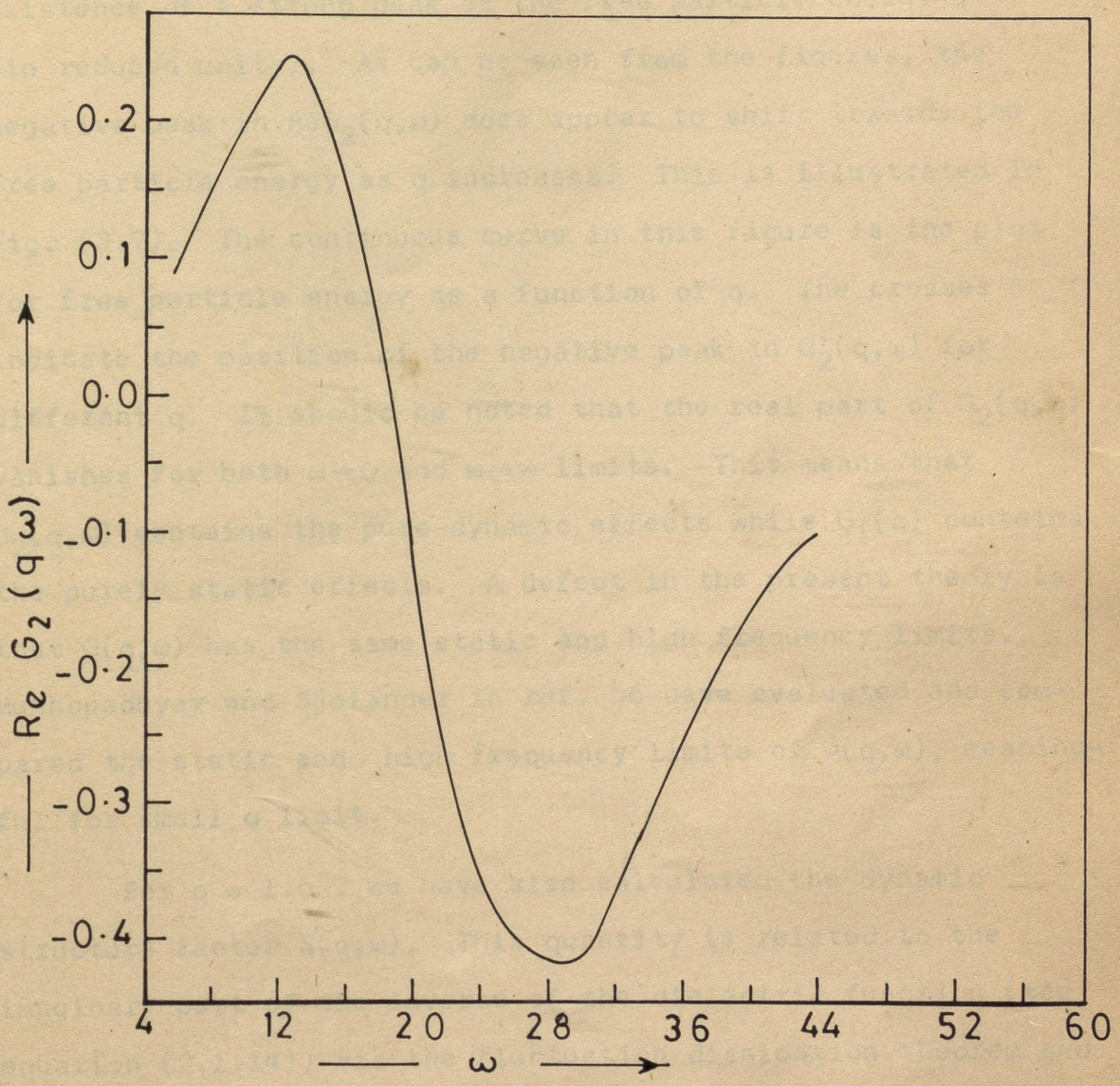


Fig. 3·6 : Real part of $G_2(q,\omega)$ for $q = 5{\cdot}0$ and $r_s = 2$ as a function of ω.

from his exact treatment of $G(q,\omega)$ for very large q, the existence of a strong peak at the free particle energy q^2 (in reduced units), As can be seen from the figures, the negative peak in $ReG_2(q,\omega)$ does appear to shift towards the free particle energy as q increases. This is illustrated in Fig. (3.7). The continuous curve in this figure is the plot for free particle energy as a function of q. The crosses indicate the position of the negative peak in $G_2'(q,\omega)$ for different q. It should be noted that the real part of $G_2(q,\omega)$ vanishes for both $\omega \to 0$ and $\omega \to \infty$ limits. This means that $G_2(\underset{\sim}{q},\omega)$ contains the pure dynamic effects while $G_1(\underset{\sim}{q})$ contains the purely static effects. A defect in the present theory is that $G(\underset{\sim}{q},\omega)$ has the same static and high frequency limits. Mukhopadhyay and Sjolander in ref. 56 have evaluated and compared the static and high frequency limits of $G(\underset{\sim}{q},\omega)$, meaningful for small q limit.

For $q = 1.6$, we have also calculated the dynamic structure factor $S(q,\omega)$. This quantity is related to the imaginary part of the inverse of the dielectric function (see equation (2.1.14)) via the fluctuation dissipation theorem and so in turn is proportional to the $Q''(q,\omega)$. To calculate $Q''(q,\omega)$, we have used the static local field factor of STLS[31] for $G_1(q)$. In figure (3.8) we present our results for $Q^{r''}(q,\omega)$ (curve 1) as a function of ω for $q = 1.6$. Curve 2 in the figure is a plot of $Q''(q,\omega)$ in the RPA and curve 3 is

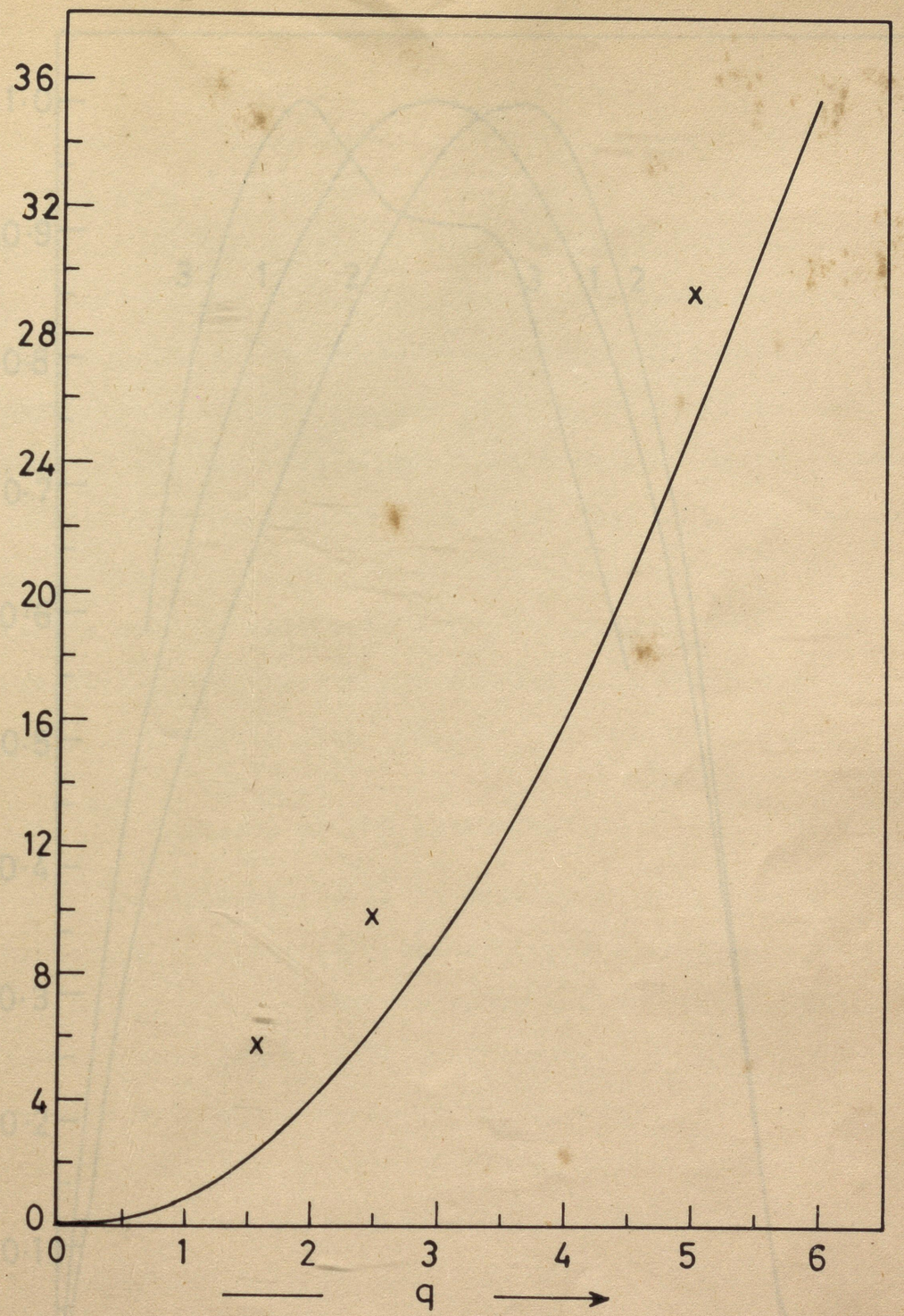


Fig. 3·7 : Solid curve is a plot for free particle energy q^2 vs. q. The crosses indicate position of the negative peak in Re $G_2(q,\omega)$ for different q values.

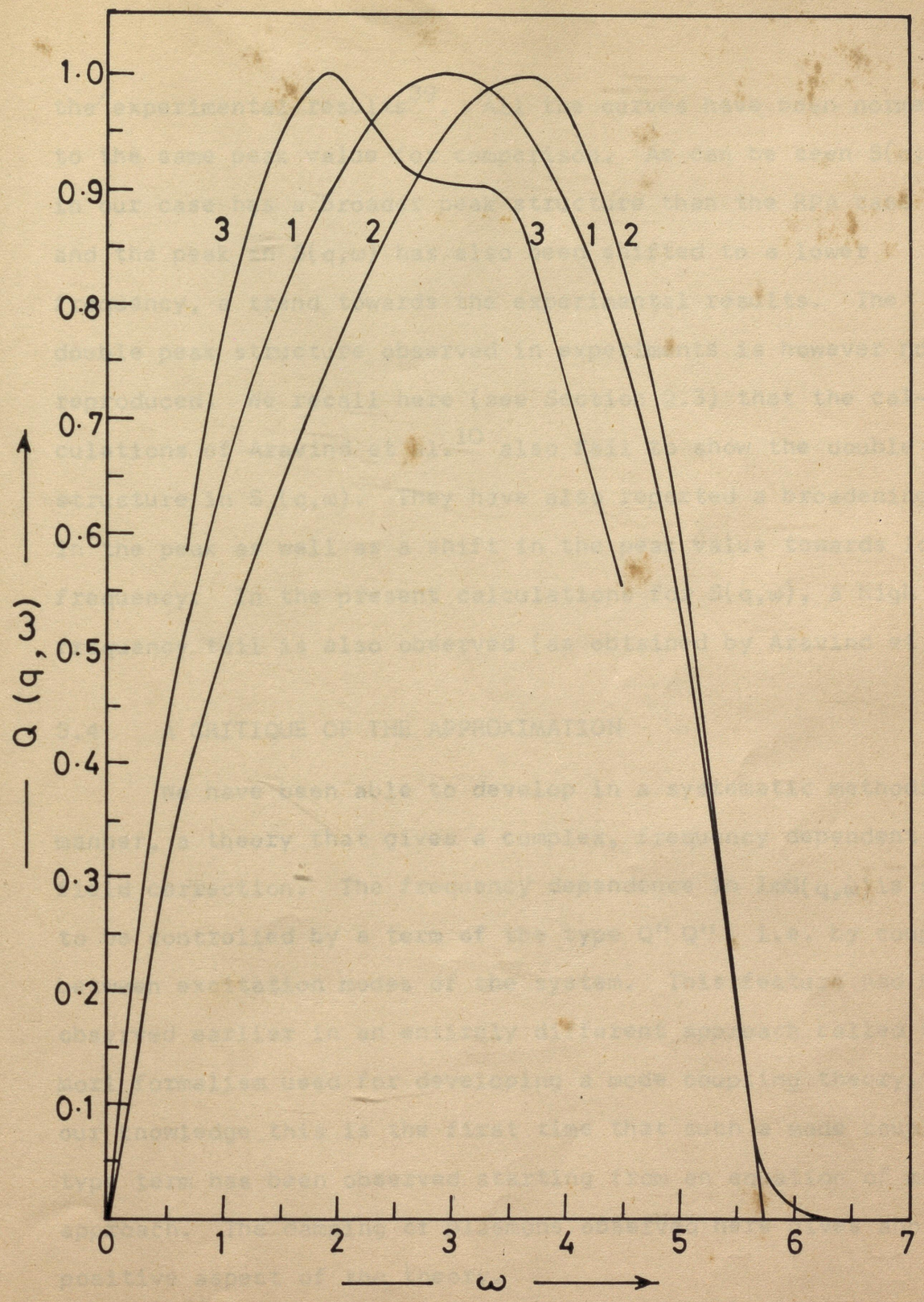


Fig. 3·8 : Plot of $Q''(q,\omega)$ vs. ω for $q = 1{\cdot}6$ and $r_s = 2$.
Curve 1 : present calculations; Curve 2 : RPA;
Curve 3 : experimental results.

the experimental results[39]. All the curves have been normalised to the same peak value for comparison. As can be seen $S(q,\omega)$ in our case has a broader peak structure than the RPA case and the peak in $S(q,\omega)$ has also been shifted to a lower frequency, a trend towards the experimental results. The double peak structure observed in experiments is however not reproduced. We recall here (see Section 2.3) that the calculations of Aravind et al.[10] also fail to show the double peak structure in $S(q,\omega)$. They have also reported a broadening in the peak as well as a shift in the peak value towards lower frequency. In the present calculations for $S(q,\omega)$, a high frequency tail is also observed (as obtained by Aravind et al.[10]).

3.4 A CRITIQUE OF THE APPROXIMATION

We have been able to develop in a systematic methodical manner, a theory that gives a complex, frequency dependent local field correction. The frequency dependence in $\mathrm{Im}G(q,\omega)$ is seen to be controlled by a term of the type $Q'' Q''$, i.e. by coupling between excitation modes of the system. This feature had been observed earlier in an entirely different approach called the Mori formalism used for developing a mode coupling theory. To our knowledge this is the first time that such a mode coupling type term has been observed starting from an equation of motion approach. The damping of plasmons observed here gives another positive aspect of the theory.

In the static limit the expression for the local field is designed to reduce to that obtained by STLS[31] ; hence we get the same values for compressibility as reported by them. The third moment sum rule is also not satisfied exactly here. A major disadvantage of the present approximation is the fact that $G(\underset{\sim}{q},\omega)$ gives the same static and high frequency results. Also we are not able to reproduce the experimentally observed double peak structure for $S(q,\omega)$. The ad-hoc nature of the approximation for the vertex function $\bar{h}$ could be responsible for these drawbacks. It is hence essential to obtain an expression for $\bar{h}$ in a more systematic manner. We develop such an approximation in the next chapter.

CHAPTER 4

AN IMPROVED APPROXIMATION FOR $G(q,\omega)$

We make an attempt here to improve upon the approximation made in the earlier chapter for $\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$. Instead of the ad-hoc approximation discussed there, we develop here a method for obtaining the vertex function starting from its definition and using linear response theory. To understand the content of the approximation, we also use two different approaches to obtain $G(\underset{\sim}{q},\omega)$ where higher order correlations are included. The sectionwise distribution of this chapter is given below.

In section (4.1) we develop an expression for the vertex function (appearing in the integral equation for the time-ordered function) using linear response theory. Section (4.2) gives the results of the calculations carried out in small q limit for the local field correction $G(q,\omega)$ in this approximation. Section (4.3) elaborates on a method for obtaining $C^{(2)}$ based on its extraction from the equation of motion for $f^{(2)}$. In section (4.4) we define a response function corresponding to $D^{(2)}$ in the presence of an external field and then use its equation of motion to obtain the local field $G(q,\omega)$. Working within the equation of motion approach, in section (4.5), we obtain an expression, hitherto unknown, for $f^{(2)eq}$. We conclude the chapter by section (4.6) which gives in brief a discussion based on this study.

4.1 DETERMINATION OF $\bar{D}^{(2)}$ VIA LINEAR RESPONSE THEORY

As discussed in Chapter 3, using the integral equation for the time ordered function, we get an expression for $D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ from equations (3.2.8), (3.2.9) and (3.2.2a),

$$D^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = D^{(2)eq}(\underset{\sim}{q},\underset{\sim}{q}') + i\hbar \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} e^{i\omega'\delta} \epsilon^{-1}(\underset{\sim}{q},\omega-\omega')\,\epsilon^{-1}(\underset{\sim}{q}',\omega')\,\bar{\pi}^{o}(\underset{\sim}{q},\underset{\sim}{q}';\omega-\omega',\omega') \qquad (4.1.1)$$

where,

$$i\hbar\,\bar{\pi}^{o}(\underset{\sim}{q}_1,\underset{\sim}{q}_2;\omega_1,\omega_2) = \iint dt_1\,dt_2\, e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} \overline{\langle T\{\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t_1)\,\hat{\tilde{\rho}}(\underset{\sim}{q}_2,t_2)\}\rangle_0} \qquad (4.1.2)$$

Here,

$$\hat{\tilde{\rho}}(\underset{\sim}{q},t) = \hat{\rho}(\underset{\sim}{q},t) - \langle\hat{\rho}(\underset{\sim}{q},t)\rangle_{eq} \qquad (4.1.3)$$

In the preceding chapter, we had used an ad-hoc approximation suggested by Singwi et al. (SSTL)[6] for $\bar{\pi}^{o}$. Here we use linear response theory to get an expression for $\bar{\pi}^{o}$ and hence for $\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ and $G(\underset{\sim}{q},\omega)$. Since $\bar{\pi}^{o}$ is the change in π^{o} of a non-interacting system in the presence of an external field which must now be screened, we write the total Hamiltonian H for this system, as a sum of H_0, the Hamiltonian for the non-interacting system and H_1, that due to the external field which is screened by the free electrons themselves. Assuming that the field is the Hartree screened field, we have in the mean field approach,

$$H_1 = \int d\underset{\sim}{x}\; \hat{\rho}(\underset{\sim}{x},t)\,\phi_{eff}(\underset{\sim}{x},t), \qquad (4.1.3a)$$

where in Fourier space the effective potential is given by,

$$\Phi_{eff}(\underset{\sim}{q},\omega) = \Phi_{ext}(\underset{\sim}{q},\omega) + v(q)\bar{n}(\underset{\sim}{q},\omega) . \qquad (4.1.3b)$$

Let,

$$\hat{\rho}^0(\underset{\sim}{x},t) = e^{iH_0t/\hbar}\,\hat{\rho}(\underset{\sim}{x})\,e^{-iH_0t/\hbar} ,$$

and also for any operator $\hat{O}^0(\underset{\sim}{x},t)$ let the time dependence be given by,

$$\hat{O}^0(\underset{\sim}{x},t) = e^{iH_0t/\hbar}\,\hat{O}(\underset{\sim}{x})\,e^{-iH_0t/\hbar} .$$

Then assuming that the system was unperturbed at $t = -\infty$, we have,

$$\hat{O}(\underset{\sim}{x},t) = U^+(t,-\infty)\,\hat{O}^0(\underset{\sim}{x}t)\,U(t,-\infty) . \qquad (4.1.4a)$$

U is the time evolution operator for H_1 and assuming linear response, is given to first order in perturbation by,

$$U(t,-\infty) = 1 - \frac{i}{\hbar}\int_{-\infty}^{t} dt' \int d\underset{\sim}{x}'\; \hat{\rho}^0(\underset{\sim}{x}',t')\,\phi_{eff}(\underset{\sim}{x}',t') . \qquad (4.1.4b)$$

This means we can write to linear order in the external potential,

$$\hat{O}(\underset{\sim}{x},t) = \hat{O}^0(\underset{\sim}{x},t) - \frac{i}{\hbar}\int_{-\infty}^{t} dt' \int d\underset{\sim}{x}' \left[\hat{O}^0(\underset{\sim}{x},t),\hat{\rho}^0(\underset{\sim}{x}',t')\right]_- \Phi_{eff}(\underset{\sim}{x}',t') . \qquad (4.1.5)$$

We use these linear response equations to evaluate $\bar{\pi}^0$ which can be written as,

$$i\hbar\,\bar{\Pi}^0(1,2) = \theta(t_1-t_2)\overline{\langle\hat{\tilde{\rho}}(1)\hat{\tilde{\rho}}(2)\rangle_0} + \theta(t_2-t_1)\overline{\langle\hat{\tilde{\rho}}(2)\hat{\tilde{\rho}}(1)\rangle_0} , \qquad (4.1.6)$$

where $1 \equiv (r_1,t_1)$; $2 \equiv (r_2,t_2)$ etc., and as before the bars indicate deviation from equilibrium. Using equation (4.1.5) and retaining terms only to the first order in Φ_{eff}, we have,

$$i\hbar \overline{\langle \hat{\hat{\rho}}(1)\hat{\hat{\rho}}(2)\rangle}_0 = \int_{-\infty}^{\infty} dt' \int d\underset{\sim}{q}' \; \Phi_{eff}(-\underset{\sim}{q}', t')$$

$$\cdot \{\theta(t_1 - t')\langle 0|[\hat{\hat{\rho}}^0(\underset{\sim}{q}_1, t_1), \hat{\hat{\rho}}^0(\underset{\sim}{q}', t')]_- \hat{\hat{\rho}}^0(\underset{\sim}{q}_2, t_2)|0\rangle$$

$$+ \theta(t_2 - t')\langle 0|\hat{\hat{\rho}}^0(\underset{\sim}{q}_1, t_1)[\hat{\hat{\rho}}^0(\underset{\sim}{q}_2, t_2), \hat{\hat{\rho}}^0(\underset{\sim}{q}', t')]_-|0\rangle\}, \quad (4\cdot1\cdot7)$$

where $|0\rangle$ represents the non-interacting ground state (at $T = 0$). Since all the operators are in the interaction representation we can write,

$$a_{\underset{\sim}{k}\sigma}(t) = e^{iH_0 t/\hbar} a_{\underset{\sim}{k}\sigma} e^{-iH_0 t/\hbar} = e^{-i\epsilon_k^0 t/\hbar} \cdot a_{\underset{\sim}{k}\sigma}, \quad (4\cdot1\cdot8)$$

where ϵ_k^0 is the free particle energy given by $\hbar^2 k^2/2m$. Using this,

$$\hat{\rho}(\underset{\sim}{q}, t) = \sum_{\underset{\sim}{k}\sigma} a^\dagger_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t),$$

$$= \sum_{\underset{\sim}{k}\sigma} e^{-i\hbar(\underset{\sim}{k}\cdot\underset{\sim}{q})/m \cdot t} a^\dagger_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}. \quad (4\cdot1\cdot9)$$

Writing the time dependence of the density operators in this way we have,

$$i\hbar \overline{\langle \hat{\rho}(\underset{\sim}{q}_1, t_1)\hat{\rho}(\underset{\sim}{q}_2, t_2)\rangle}_0 = \int_{-\infty}^{\infty} dt' \int d\underset{\sim}{q}' \; \Phi_{eff}(-\underset{\sim}{q}', t')$$

$$\cdot \sum_{\substack{\underset{\sim}{k}'\sigma' \\ \underset{\sim}{k}_1\sigma_1, \underset{\sim}{k}_2\sigma_2}} e^{-i\hbar \frac{\underset{\sim}{k}'\cdot\underset{\sim}{q}'}{m} t'} e^{-i\hbar \frac{\underset{\sim}{k}_1\cdot\underset{\sim}{q}'}{m} t_1} e^{-i\hbar \frac{\underset{\sim}{k}_2\cdot\underset{\sim}{q}'}{m} t_2}$$

$$\cdot \Big[\theta(t_1 - t')\{-\langle 0|a^\dagger_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'} a_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'} a^\dagger_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1} a_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1} a^\dagger_{\underset{\sim}{k}_2-\underset{\sim}{q}_2/2\sigma_2} a_{\underset{\sim}{k}_2+\underset{\sim}{q}_2/2\sigma_2}|0\rangle$$

$$+ \langle 0|a^\dagger_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1} a_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1} a^\dagger_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'} a_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'} a^\dagger_{\underset{\sim}{k}_2-\underset{\sim}{q}_2/2\sigma_2} a_{\underset{\sim}{k}_2+\underset{\sim}{q}_2/2\sigma_2}|0\rangle\}$$

$$+ \theta(t_2 - t')\{\langle 0|a^\dagger_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1} a_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1} a^\dagger_{\underset{\sim}{k}_2-\underset{\sim}{q}_2/2\sigma_2} a_{\underset{\sim}{k}_2+\underset{\sim}{q}_2/2\sigma_2} a^\dagger_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'} a_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'}|0\rangle$$

$$- \langle 0|a^\dagger_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1} a_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1} a^\dagger_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'} a_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'} a^\dagger_{\underset{\sim}{k}_2-\underset{\sim}{q}_2/2\sigma_2} a_{\underset{\sim}{k}_2+\underset{\sim}{q}_2/2\sigma_2}|0\rangle\}\Big] \quad (4\cdot1\cdot10)$$

The matrix elements with respect to the ground state $|0\rangle$ can be evaluated by first writing the creation and destruction operators, $a^\dagger_{\underset{\sim}{k}\sigma}$ and $a_{\underset{\sim}{k}\sigma}$, in terms of the corresponding particle

and hole operators and then using the latter's commutation properties. Thus we write,

$$a_{\underset{\sim}{k}\sigma} = \theta(k-k_F)\, p_{\underset{\sim}{k}\sigma} + \theta(k_F-k)\, h^{+}_{-\underset{\sim}{k}\sigma} \qquad (4.1.11)$$

and use the fact that,

$$\left.\begin{aligned} &\langle 0|\, p^{+}_{\underset{\sim}{k}\sigma} = p_{\underset{\sim}{k}\sigma}\,|0\rangle = 0 \;; \\ &\{p^{+}_{\underset{\sim}{k}\sigma}, p_{\underset{\sim}{k}'\sigma'}\} = \delta_{\underset{\sim}{k},\underset{\sim}{k}'}\,\delta_{\sigma,\sigma'} = \{h^{+}_{\underset{\sim}{k}\sigma}, h_{\underset{\sim}{k}'\sigma'}\} \;; \\ &\text{and} \quad \{p_{\underset{\sim}{k}\sigma}, h_{\underset{\sim}{k}'\sigma'}\} = \{p^{+}_{\underset{\sim}{k}\sigma}, h_{\underset{\sim}{k}'\sigma'}\} = 0 \quad \text{etc.} \end{aligned}\right\} \qquad (4.1.12)$$

Thus in general we get,

$$\begin{aligned} &\langle 0|\, a^{+}_{k_1\sigma_1} a_{k_2\sigma_2} a^{+}_{k_3\sigma_3} a_{k_4\sigma_4} a^{+}_{k_5\sigma_5} a_{k_6\sigma_6}\,|0\rangle \\ &= n^{0}_{k_1\sigma_1}(1-n^{0}_{k_2\sigma_2})(1-n^{0}_{k_4\sigma_4})\,\delta_{16}\,\delta_{23}\,\delta_{45} \\ &+ n^{0}_{k_1\sigma_1}(1-n^{0}_{k_2\sigma_2})\,n^{0}_{k_5\sigma_5}\,\delta_{14}\,\delta_{23}\,\delta_{56} \\ &+ n^{0}_{k_1\sigma_1}(1-n^{0}_{k_2\sigma_2})\,n^{0}_{k_3\sigma_3}\,\delta_{16}\,\delta_{34}\,\delta_{25} \\ &- n^{0}_{k_1\sigma_1}(1-n^{0}_{k_2\sigma_2})\,n^{0}_{k_3\sigma_3}\,\delta_{14}\,\delta_{25}\,\delta_{36} \\ &+ n^{0}_{k_1\sigma_1}\,n^{0}_{k_3\sigma_3}(1-n^{0}_{k_4\sigma_4})\,\delta_{12}\,\delta_{36}\,\delta_{45} \\ &+ n^{0}_{k_1\sigma_1}\,n^{0}_{k_5\sigma_5}\,n^{0}_{k_3\sigma_3}\,\delta_{12}\,\delta_{34}\,\delta_{56}\,. \end{aligned} \qquad (4.1.13)$$

Here $n^{0}_{\underset{\sim}{k}\sigma}$ is the momentum distribution for the non-interacting Fermi system and $\delta_{12} = \delta(\underset{\sim}{r}_1-\underset{\sim}{r}_2)\,\delta(t_1-t_2)$ etc. Using this matrix element, we can evaluate the function in equation (4.1.10) to get,

$$\begin{aligned} \overline{\langle \hat{s}(\underset{\sim}{q}_1,t_1)\,\hat{s}(\underset{\sim}{q}_2,t_2)\rangle_0} &= \frac{i}{\hbar}\int_{-\infty}^{\infty} dt' \Big[\phi_{\text{eff}}(\underset{\sim}{q}_1+\underset{\sim}{q}_2,\, t_1-t') \\ &\cdot \Big[\Big\{ e^{i\hbar\,\frac{\underset{\sim}{q}_1\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{2m}t'} - e^{-i\hbar\,\frac{\underset{\sim}{q}_1\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{2m}t'}\Big\} \sum_{\underset{\sim}{k}_2\sigma_2} e^{-i\hbar\,\frac{\underset{\sim}{k}_2\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{m}t' - i\hbar\,\frac{\underset{\sim}{k}_1\cdot\underset{\sim}{q}_1}{m}(t_2-t_1)} \\ &\cdot n_{\underset{\sim}{k}_2+\underset{\sim}{q}_2/2\sigma_2}\,(1-n_{\underset{\sim}{k}_2-\underset{\sim}{q}_2/2\sigma_2}) \\ &+ N\,\delta_{\underset{\sim}{q}_2,0} \sum_{\underset{\sim}{k}_1\sigma_1} e^{-i\hbar\,\frac{\underset{\sim}{k}_1\cdot\underset{\sim}{q}_1}{m}t'} \,(n_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1} - n_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1})\Big] \end{aligned}$$

$$+ \Phi_{eff}(\underset{\sim}{q}_1+\underset{\sim}{q}_2, t_2-t')\Big[\Big\{ e^{i\hbar \frac{\underset{\sim}{q}_2\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{m} t'} - e^{-i\hbar \frac{\underset{\sim}{q}_2\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{m} t'}\Big\}$$

$$\cdot \sum_{\underset{\sim}{k}_1\sigma_1} e^{-i\hbar \frac{\underset{\sim}{k}_1\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)}{m} t' - i\hbar \frac{\underset{\sim}{k}_2\cdot\underset{\sim}{q}_2}{m}(t_1-t_2)} \cdot n_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1}(1-n_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1})$$

$$+ N\delta_{q_1,0}\sum_{\underset{\sim}{k}_2\sigma_2} e^{-i\hbar \frac{\underset{\sim}{k}_2\cdot\underset{\sim}{q}_2}{m} t'}\left(n_{\underset{\sim}{k}_2+\underset{\sim}{q}_2/2\sigma_2} - n_{\underset{\sim}{k}_2-\underset{\sim}{q}_2/2\sigma_2}\right)\Big]\Big]. \quad (4.1.14)$$

An expression for $\overline{\langle \hat{\rho}(\underset{\sim}{q}_2,t_2)\hat{\rho}(\underset{\sim}{q}_1,t_1)\rangle}$ also follows from (4.1.14) by appropriate interchange of the variables $\underset{\sim}{q}_1, t_1$ and $\underset{\sim}{q}_2, t_2$. Working in an identical fashion we can get an expression for $\overline{\langle \hat{\rho}(\underset{\sim}{q}_1,t_1)\rangle_0}$,

$$\overline{\langle \hat{\rho}(\underset{\sim}{q}_1,t_1)\rangle_0} = \frac{i}{\hbar}\int dt' \Phi_{eff}(\underset{\sim}{q},t')\sum_{\underset{\sim}{k}_1\sigma_1} e^{i\hbar \frac{\underset{\sim}{k}_1\cdot\underset{\sim}{q}_1}{m}(t'-t_1)} \cdot \left(n_{\underset{\sim}{k}_1+\underset{\sim}{q}_1/2\sigma_1} - n_{\underset{\sim}{k}_1-\underset{\sim}{q}_1/2\sigma_1}\right), \quad (4.1.15)$$

from which an expression for $\overline{\langle \hat{\rho}(\underset{\sim}{q}_2,t_2)\rangle_0}$ can be written down easily. Using these expressions we can get $\overline{\pi^0(1,2)}$ from equation (4.1.6),

$$i\hbar\,\overline{\pi^0(1,2)} = \theta(t_1-t_2)\overline{\langle \hat{\rho}(\underset{\sim}{q}_1,t_1)\hat{\rho}(\underset{\sim}{q}_2,t_2)\rangle_0} + \theta(t_2-t_1)\overline{\langle \hat{\rho}(\underset{\sim}{q}_2,t_2)\hat{\rho}(\underset{\sim}{q}_1,t_1)\rangle_0}$$

$$- \overline{\langle \hat{\rho}(\underset{\sim}{q}_1,t_1)\rangle_0}\langle \hat{\rho}(\underset{\sim}{q}_2,t_2)\rangle_0^{eq} - \langle \hat{\rho}(\underset{\sim}{q}_1,t_1)\rangle_0^{eq}\overline{\langle \rho(\underset{\sim}{q}_2,t_2)\rangle_0}. \quad (4.1.16)$$

Taking the temporal Fourier transform with respect to both time coordinates t_1 and t_2, we get,

$$i\hbar\,\bar{\pi}^0(q_1,q_2;\omega_1,\omega_2) = \int_{-\infty}^{\infty} dt_1\,dt_2\, e^{i\omega_1 t_1} e^{i\omega_2 t_2}\,\bar{\pi}^0(q_1,q_2;t_1,t_2),$$

$$= \frac{i}{\hbar}\Phi_{eff}(\underset{\sim}{q}_1+\underset{\sim}{q}_2,\ \omega_1+\omega_2)$$

$$\Big[\sum_{\underset{\sim}{k}_2\sigma_2}\Big\{\frac{1}{\omega_1+\omega_2-\frac{\hbar}{m}(\underset{\sim}{k}_2-\frac{\underset{\sim}{q}_1}{2})\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)+i\Delta} - \frac{1}{\omega_1+\omega_2-\frac{\hbar}{m}(\underset{\sim}{k}_2+\frac{\underset{\sim}{q}_1}{2})\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)+i\Delta}\Big\}\chi^{co}_{\underset{\sim}{k}_2\sigma_2}(\underset{\sim}{q}_2,\omega_2)$$

$$+\sum_{\underset{\sim}{k}_1\sigma_1}\Big\{\frac{1}{\omega_1+\omega_2-\frac{\hbar}{m}(\underset{\sim}{k}_1-\frac{\underset{\sim}{q}_2}{2})\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)+i\Delta} - \frac{1}{\omega_1+\omega_2-\frac{\hbar}{m}(\underset{\sim}{k}_1+\frac{\underset{\sim}{q}_2}{2})\cdot(\underset{\sim}{q}_1+\underset{\sim}{q}_2)+i\Delta}\Big\}\chi^{co}_{\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}_1,\omega_1)\Big], \quad (4.1.17)$$

where $\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)$ is defined as,

$$\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega) = \frac{1}{\hbar V}\left[\frac{n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(1-n^0_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})}{\omega+i\delta-\frac{\hbar}{m}(\underset{\sim}{k}.\underset{\sim}{q})} - \frac{n^0_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(1-n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma})}{\omega-i\delta-\frac{\hbar}{m}(\underset{\sim}{k}.\underset{\sim}{q})}\right].$$

Then from equation (4.1.1) we have,

$$\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = i\hbar\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,e^{i\omega'\delta}\,\epsilon^{c-1}(\underset{\sim}{q},\omega-\omega')\,\epsilon^{c-1}(\underset{\sim}{q}',\omega')\,\bar{\Pi}^0(\underset{\sim}{q},\underset{\sim}{q}',\omega-\omega',\omega'),$$

$$= i\phi_{eff}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\Bigg[\sum_{\underset{\sim}{k}_1\sigma_1}\left\{\frac{1}{\omega-\frac{\hbar}{m}(\underset{\sim}{k}_1+\frac{\underset{\sim}{q}'}{2})\cdot(\underset{\sim}{q}+\underset{\sim}{q}')+i\Delta}-\frac{1}{\omega-\frac{\hbar}{m}(\underset{\sim}{k}_1-\frac{\underset{\sim}{q}}{2})\cdot(\underset{\sim}{q}+\underset{\sim}{q}')+i\Delta}\right\}$$

$$\cdot\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,e^{i\omega'\delta}\,\epsilon^{c-1}(\underset{\sim}{q}',\omega')\,\chi^c_{\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q},\omega-\omega')$$

$$+\sum_{\underset{\sim}{k}_2\sigma_2}\left\{\frac{1}{\omega-\frac{\hbar}{m}(\underset{\sim}{k}_2+\frac{\underset{\sim}{q}'}{2})\cdot(\underset{\sim}{q}+\underset{\sim}{q}')+i\Delta}-\frac{1}{\omega-\frac{\hbar}{m}(\underset{\sim}{k}_2-\frac{\underset{\sim}{q}'}{2})\cdot(\underset{\sim}{q}+\underset{\sim}{q}')+i\Delta}\right\}$$

$$\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,e^{i\omega'\delta}\,\epsilon^{c-1}(\underset{\sim}{q},\omega')\,\chi^c_{\underset{\sim}{k}_2\sigma_2}(\underset{\sim}{q}',\omega-\omega')\Bigg]. \qquad (4.1.18)$$

As is very clear from the above expression, due to the systematic development, the $\bar{D}^{(2)}$ obtained here is symmetric with respect to exchange of $\underset{\sim}{q}$ and $\underset{\sim}{q}'$ variables, as required by the definition of $\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$. The quantity that we are interested in, for determination of the response function $\chi^r(q,\omega)$, is,

$$\frac{1}{nV}\sum_{\underset{\sim}{q}'}v(\underset{\sim}{q}')\,\bar{\bar{D}}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$= \phi_{eff}(\underset{\sim}{q},\omega)\,\frac{1}{nV}\sum_{\underset{\sim}{q}'}v(\underset{\sim}{q}')\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,e^{i\omega'\delta}\,\epsilon^{c-1}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega')\,\epsilon^{c-1}(\underset{\sim}{q}',\omega')$$

$$\cdot(-i\hbar)\sum_{\underset{\sim}{k}\sigma}\Big[\left\{\bar{D}_1^{-1}(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega)-\bar{D}_1^{-1}(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega)\right\}\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega')$$

$$+\left\{\bar{D}_1^{-1}(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega)-\bar{D}_1^{-1}(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega)\right\}\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega')\Big],$$

where,

$$D_1(\underset{\sim}{k},\underset{\sim}{q},\omega) = \hbar\omega+i\delta-\frac{\hbar^2}{m}(\underset{\sim}{k}.\underset{\sim}{q}) \qquad (4.1.19)$$

Since we have used the random phase approximation while

evaluating $\bar{D}^{(2)}$, in the above equation also we use the RPA form for the dielectric function, so that,

$$\chi^{c}_{RPA}(\underset{\sim}{q},\omega) = \frac{\chi^{co}(\underset{\sim}{q},\omega)}{1-v(q)\chi^{co}(\underset{\sim}{q},\omega)} = \frac{\chi^{co}(\underset{\sim}{q},\omega)}{\epsilon^{c}(\underset{\sim}{q},\omega)} .$$

Replacing $\underset{\sim}{q}'$ by $\underset{\sim}{q}-\underset{\sim}{q}'$ in one of the terms and using the following symmetry relations, (discussed in Appendix I),

$$\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},-\omega) = \chi^{co}_{-\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega) = \chi^{co}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q},\omega) , \quad (4\cdot1\cdot20a)$$

and

$$\epsilon^{c-1}(\underset{\sim}{q},-\omega) = \epsilon^{c-1}(\underset{\sim}{q},\omega) , \quad (4\cdot1\cdot20b)$$

we have,

$$\frac{1}{nV}\sum_{\underset{\sim}{q}'} v(q')\,\bar{D}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}',\omega)\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$= \Phi_{eff}(\underset{\sim}{q},\omega)\frac{1}{nV}\Bigg[\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$\sum_{\underset{\sim}{k}\sigma}\left\{D_1^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega\right)-D_1^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega\right)\right\}F_{-\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega)$$

$$+\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}-\underset{\sim}{q}')\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}-\underset{\sim}{q}',\omega)\sum_{\underset{\sim}{k}\sigma}\left\{D_1^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega\right)-D_1^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega\right)\right\}$$

$$\cdot F_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\Bigg] \quad (4\cdot1\cdot21)$$

$$= \Phi_{eff}(q,\omega)\,\chi^{A}(\underset{\sim}{q},\omega) , \quad (4\cdot1\cdot21a)$$

where,

$$F_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = (-i\hbar)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,\epsilon^{c-1}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega')\,\epsilon^{c-1}(\underset{\sim}{q}',\omega')\,e^{-i\omega'\delta}\,\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega') \quad (4\cdot1\cdot22)$$

Substituting this expression in equation (3.1.9) we obtain,

$$\chi^{r}(\underset{\sim}{q},\omega) = \frac{\chi^{ro}(\underset{\sim}{q},\omega)+\chi^{A}(\underset{\sim}{q},\omega)}{1-v(q)\{\chi^{ro}(q,\omega)+\chi^{A}(q,\omega)\}-\frac{1}{nV}\sum_{\underset{\sim}{q}'} v(q')\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)} . \quad (4\cdot1\cdot23)$$

The expression for $\chi^{A}(\underset{\sim}{q},\omega)$ can be further simplified. Again using the RPA expression for $\epsilon^{c}(\underset{\sim}{q},\omega)$, we can split $F_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$

into two terms as given below,

$$F_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = (-i\hbar)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\;\frac{\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega')}{\epsilon^{c}(\underset{\sim}{q}',\omega')}\;e^{-i\omega'\delta}$$

$$+(-i\hbar)\,v(\underset{\sim}{q}-\underset{\sim}{q}')\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\;\frac{\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega')}{\epsilon^{c}(\underset{\sim}{q}',\omega')}\;\chi^{c}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega')\,e^{-i\omega'\delta}$$

In the above equation the first term can be written as,

$$(-i\hbar)\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\;\frac{\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega')}{\epsilon^{c}(\underset{\sim}{q}',\omega')}\;e^{-i\omega'\delta} = (-i\hbar)\sum_{\underset{\sim}{k}'\sigma'}\oint\frac{d\omega'}{2\pi}\;\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',\omega')$$

$$= -\frac{1}{\hbar}\sum_{\underset{\sim}{k}'\sigma'}\left\langle\hat{\hat{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}')\;\hat{\hat{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')\right\rangle_{eq},$$

$$= -\frac{1}{\hbar}\sum_{\underset{\sim}{k}'\sigma'}f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') - \frac{1}{\hbar}\,n_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma}\,. \qquad (4.1.24)$$

Here we have used the relations between the retarded and causal response functions and the correlation functions as discussed in Appendix I (equation (A.1.17)). All the quantities here are within the RPA.

In the second term, we use the spectral representation for the causal response function (equation (3.3.2), so that the second term now reads,

$$-\frac{\hbar}{\pi}\int_{0}^{\infty}d\omega_1\;\mathrm{Im}\,\chi^{r}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)\sum_{\underset{\sim}{k}'\sigma'}\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi i}\;e^{-i\omega'\delta}$$

$$\cdot\,\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',\omega')\left\{\frac{1}{\omega-\omega'+i\delta_1-\omega_1}-\frac{1}{\omega-\omega'-i\delta_1+\omega_1}\right\}$$

$$= -\frac{\hbar}{\pi}\int_{0}^{\infty}d\omega_1\;\mathrm{Im}\,\chi^{r}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)\sum_{\underset{\sim}{k}'\sigma'}\left(-\frac{1}{\pi}\right)\int_{0}^{\infty}d\omega_2\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi i}\cdot e^{-i\omega'\delta}$$

$$\cdot\left\{\frac{\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}',\omega_2)}{\omega'-\omega_2+i\delta_2}-\frac{\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',\omega_2)}{\omega'+\omega_2-i\delta_2}\right\}$$

$$\cdot\left\{\frac{1}{\omega-\omega'+i\delta_1-\omega_1}-\frac{1}{\omega-\omega'-i\delta_1+\omega_1}\right\},$$

$$= \frac{1}{\pi}\int_0^\infty d\omega_1 \, \mathrm{Im}\, \chi^r(\underset{\sim}{q}-\underset{\sim}{q}', \omega_1) \sum_{\underset{\sim}{k}'\sigma'} \Big[\chi^c_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', \omega+\omega_1)$$

$$- \frac{1}{\pi}\int_0^\infty d\omega_2 \Big\{ \frac{\mathrm{Im}\, \chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}', \omega_2)}{\omega-\omega_2-\omega_1+i\delta} - \frac{\mathrm{Im}\, \chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', \omega_2)}{\omega-\omega_2+\omega_1+i\delta} \Big\} \Big],$$

$$= \frac{1}{\pi}\sum_{\underset{\sim}{k}'\sigma'} \int_0^\infty d\omega_1 \Big[\mathrm{Im}\, \chi^r(\underset{\sim}{q}-\underset{\sim}{q}', \omega_1)\, \chi^c_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', \omega+\omega_1)$$

$$+ \chi^r(\underset{\sim}{q}-\underset{\sim}{q}', \omega-\omega_1)\, \mathrm{Im}\, \chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', \omega_1) \Big],$$

$$= F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \,/\, v(\underset{\sim}{q}-\underset{\sim}{q}') \quad . \qquad (4.1.25)$$

Here the ω'-integral in the second line has been performed using contour integration as used earlier in Section (3.3) and described in Appendix III (equation (A.3.3)). To get the final result we have used the spectral representation given in Appendix I for $\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ and $\chi^c_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ (equations (A.1.18) and (A.1.19)); we then have,

$$F_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) = -\frac{1}{V}\sum_{\underset{\sim}{k}'\sigma'} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(q) - \frac{1}{V} n_{\underset{\sim}{k}-\underset{\sim}{q}'\sigma} + F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) \qquad (4.1.26)$$

Here $F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ is defined via equation (4.1.25). Substituting this into equation (4.1.21) we get,

$$\chi^A(\underset{\sim}{q}, \omega) = \chi^{A0}(\underset{\sim}{q}, \omega) + \chi^{A1}(\underset{\sim}{q}, \omega), \qquad (4.1.27)$$

where,

$$\chi^{A0}(q, \omega) = -\frac{1}{nV^2}\Big[\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\, \chi^{r0}(\underset{\sim}{q}, \underset{\sim}{q}', \omega)$$

$$\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} \Big\{ D_1^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\Big) - D_1^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\Big) \Big\} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')$$

$$+ \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}-\underset{\sim}{q}')\, \chi^{r0}(\underset{\sim}{q}, \underset{\sim}{q}-\underset{\sim}{q}', \omega) \cdot$$

$$\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} \Big\{ D_1^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\Big) - D_1^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\Big) \Big\} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \Big] \qquad (4.1.28)$$

and,

$$\chi^{A1}(q,\omega) = -\frac{1}{nV^2}\Big[\sum_{q'} v(q')\,\chi^{ro}(q,q',\omega)$$
$$\cdot\sum_{k\sigma}\Big\{D_1^{-1}\Big(k-\frac{q-q'}{2},q,\omega\Big)-D_1^{-1}\Big(k+\frac{q-q'}{2},q,\omega\Big)\Big\}F^{(1)}_{-k\sigma}(q,q',-\omega)$$
$$+\sum_{q'} v(q-q')\,\chi^{ro}(q,q-q',\omega)$$
$$\sum_{k\sigma}\Big\{D_1^{-1}\Big(k-\frac{q-q'}{2},q,\omega\Big)-D_1^{-1}\Big(k+\frac{q-q'}{2},q,\omega\Big)\Big\}F^{(1)}_{k\sigma}(q,q',\omega)\Big] \qquad (4.1.29)$$

The terms containing $n_{k-q'/2\sigma}$ and $n_{k+q'/2\sigma}$, cancel each other. This can be shown very easily using the fact that $\chi^{ro}(q,q',\omega)$ is odd with respect to q'. We define now,

$$G_0(q,\omega) = -\frac{1}{nV}\frac{1}{v(q)\chi^{ro}(q,\omega)}\sum_{q'} v(q')\{S(q-q')-1\}\chi^{ro}(q,q',\omega), \qquad (4.1.30)$$

which is the same local field factor as defined by (3.1.13) and reduces to the static value (3.1.17) in the limit of $q/\omega\to 0$ (see Section 3.1). We also define,

$$G_1(q,\omega) = -\chi^{A}(q,\omega)\,/\,\chi^{ro}(q,\omega) \qquad (4.1.31)$$

Conventionally one defines $G(q,\omega)$, the frequency and wave-vector dependent local field factor via the relation[2],

$$\chi(q,\omega) = \frac{\chi^{ro}(q,\omega)}{1-v(q)\{1-G(q,\omega)\}\chi^{ro}(q,\omega)}, \qquad (4.1.32)$$

so that,

$$G(q,\omega) = \frac{1}{v(q)}\left(\frac{1}{\chi^{r}(q,\omega)}-\frac{1}{\chi^{ro}(q,\omega)}\right)+1. \qquad (4.1.33)$$

This means, with $\chi^{r}(q,\omega)$ defined by (4.1.23), the $G(q,\omega)$

in the present case is given by,

$$G(\underset{\sim}{q},\omega) = \frac{G_1(\underset{\sim}{q},\omega)}{v(q)\chi^{ro}(\underset{\sim}{q},\omega)\{1-G_1(q,\omega)\}} + \frac{G_o(q,\omega)}{1-G_1(q,\omega)} . \quad (4\cdot1\cdot34)$$

Thus, we have again a complex, frequency and wave-vector dependent local field factor. Clearly, the static and high frequency limits are now different. In the limit of $q \to 0$, both G_o and G_1 are found to be proportional to q^2 ; further, G_o is purely real (while G_1 is complex for the more general case of $q/\omega \to 0$). This implies that the damping coefficient for long wavelength plasmons (i.e. for $q \to 0$) is determined by the imaginary part of G_1, which we consider in the following section.

4.2 CONTRIBUTIONS TO Im $G_1(q,\omega)$ IN SMALL q LIMIT

In the small q limit, $\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ has a non-zero contribution only from its real part given by,

$$\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega) \xrightarrow{q\to 0} \frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q^2}\chi^{ro}(\underset{\sim}{q},\omega) \quad (4\cdot2\cdot1)$$

Also, in our calculations for $\mathrm{Im}G_1(\underset{\sim}{q},\omega)$, we restrict ourselves to taking only contributions from the real part of the D_1 in both $\chi^{A_o}(\underset{\sim}{q},\omega)$ and $\chi^{A1}(\underset{\sim}{q},\omega)$ and $\chi^{A1}(\underset{\sim}{q},\omega)$. Since $f^{(2)eq}$ is a real quantity, the contribution to $\mathrm{Im}G_1(q,\omega)$ comes from $\chi^{A1}(\underset{\sim}{q},\omega)$ alone. For small q, we can write,

$$\mathrm{Re}\left\{D_1^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\ q,\ \omega\right)-D_1^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\ \underset{\sim}{q},\ \omega\right)\right\}$$

$$=-\frac{(\underset{\sim}{q}-\underset{\sim}{q}')\cdot\underset{\sim}{q}}{m\omega^2}\ \frac{1}{\left[1-(\hbar/m\omega)(\underset{\sim}{k}\cdot\underset{\sim}{q})\right]^2-\left[(\hbar/2m\omega)(q^2-\underset{\sim}{q}\cdot\underset{\sim}{q}')\right]^2},$$

$$=-\frac{(q^2-\underset{\sim}{q}\cdot\underset{\sim}{q}')}{m\omega^2}\left[1+\left\{\frac{2\hbar}{m\omega}(\underset{\sim}{k}\cdot\underset{\sim}{q})+\frac{\hbar^2}{4m^2\omega^2}(q^2-\underset{\sim}{q}\cdot\underset{\sim}{q}')^2-\frac{\hbar^2}{m^2\omega^2}(\underset{\sim}{k}\cdot\underset{\sim}{q})^2\right\}\right.$$

$$\left.+\left\{\frac{4\hbar^2}{m^2\omega^2}(\underset{\sim}{k}\cdot\underset{\sim}{q})^2+\frac{\hbar^3}{m^3\omega^3}(\underset{\sim}{k}\cdot\underset{\sim}{q})(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2+O(q^3)\right\}\right],\qquad (4.2.2)$$

where we have retained terms only to order q^3 because we are interested in the contribution to $\mathrm{Im}G(q,\omega)$ to lowest order in q (i.e. to order q^2). Then we have,

$$\mathrm{Im}\,G_1(\underset{\sim}{q},\omega)\xrightarrow{q\to 0}+\frac{1}{m\omega^2}\cdot\frac{v(q)}{V}\sum_{\underset{\sim}{q}'}\left[\frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}(q^2-\underset{\sim}{q}\cdot\underset{\sim}{q}')\right.$$

$$\sum_{\underset{\sim}{k}\sigma}\mathrm{Im}F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega)\left(1+\frac{\hbar^2}{4m^2\omega^2}(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2\right)$$

$$+\frac{(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2}{q'^2}\sum_{\underset{\sim}{k}\sigma}\mathrm{Im}\,F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}-\underset{\sim}{q}',\omega)\left(1+\frac{\hbar^2}{4m^2\omega^2}(\underset{\sim}{q}\cdot\underset{\sim}{q})^2\right)$$

$$-\frac{2\hbar}{m\omega}\left\{\frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}(q^2-\underset{\sim}{q}\cdot\underset{\sim}{q}')\sum_{\underset{\sim}{k}\sigma}(\underset{\sim}{k}\cdot\underset{\sim}{q})\,\mathrm{Im}\,F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega)\right.$$

$$\left.-\frac{(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2}{q'^2}\sum_{\underset{\sim}{k}\sigma}(\underset{\sim}{k}\cdot\underset{\sim}{q})\,\mathrm{Im}\,F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\right\}$$

$$+\frac{3\hbar^2}{m^2\omega^2}\left\{\frac{\underset{\sim}{q}\cdot\underset{\sim}{q}'}{q'^2}(q^2-\underset{\sim}{q}\cdot\underset{\sim}{q}')\sum_{\underset{\sim}{k}\sigma}(\underset{\sim}{k}\cdot\underset{\sim}{q})^2\,\mathrm{Im}\,F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\right.$$

$$\left.\left.-\frac{(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2}{q'^2}\sum_{\underset{\sim}{k}\sigma}(\underset{\sim}{k}\cdot\underset{\sim}{q})^2\,\mathrm{Im}\,F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\right\}\right].\qquad (4.2.3)$$

As shown in Appendix V, we can evaluate the following terms appearing in equation (4.2.3).

$$\sum_{\underset{\sim}{k}\sigma}\mathrm{Im}\,F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega)=\frac{\hbar}{\pi v(q')}\int_0^\omega d\omega_1\,Q^{r\prime\prime}(\underset{\sim}{q}',\omega_1)Q^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1);$$

(4.2.4a)

$$\sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q}) \operatorname{Im} F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega) = + \frac{m(\underset{\sim}{q}\cdot\underset{\sim}{q}')}{v(q')\pi q'^2} \int_0^\omega d\omega_1 \cdot \omega_1 Q^{r''}(\underset{\sim}{q}',\omega_1) Q^{r''}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1); \tag{4.2.4b}$$

and

$$\sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q})^2 \operatorname{Im} F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega)$$

$$= \frac{1}{v(q')} \cdot \frac{q^2}{2} \frac{\pi}{\kappa} \left[q_F^2 \{1-(\hat{q}\cdot\hat{q}')^2\} \int_0^\omega d\omega_1 Q^{r''}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1) \operatorname{Im}\left(\frac{\sum_{\underset{\sim}{k}\sigma} k^2 Q^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega_1)}{\epsilon^r(\underset{\sim}{q}',\omega_1)} \right) \right.$$

$$+ \frac{1}{q'^2} \cdot \frac{m^2}{\hbar^2} \{3(\hat{q}\cdot\hat{q}')^2 - 1\} \int_0^\omega d\omega_1 \cdot \omega_1^2 Q^{r''}(\underset{\sim}{q}',\omega_1) Q^{r''}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1)$$

$$\left. - \frac{1}{q'^2} \cdot \frac{mn}{\hbar^2} \{3(\hat{q}\cdot\hat{q}')^2 - 1\} \int_0^\omega d\omega_1 Q^{r''}(\underset{\sim}{q}',\omega_1) Q^{r''}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1) \right]. \tag{4.2.4c}$$

The t-integral can now be performed if we make a similiar expansion for $Q^{r''}(q-q',\omega)$ about q' in the small q limit as made in Section 3.3.1, i.e.,

$$Q^{r''}(\underset{\sim}{q}-\underset{\sim}{q}',\omega) = Q^{r''}(q',\omega) - \underset{\sim}{q}\cdot\underset{\sim}{\nabla}_{q'} Q^{r''}(q',\omega) . \tag{4.2.5}$$

The imaginary part of G at the plasma frequency is then given (in reduced units) by,

$$\operatorname{Im} G(\underset{\sim}{q},\omega_p) = \operatorname{Im} G_1(q,\omega_p)$$

$$= + \frac{q}{32\alpha r_s} \int_0^\infty dq' \cdot q'^2 \left[2G^{(0)}(q',q',\omega) + \frac{14}{15} q' \left(\frac{\partial}{\partial q''} G^{(0)}(q',q'',\omega) \right)_{q''\to q'} \right], \tag{4.2.6}$$

where,

$$G^{(0)}(q',q'',\omega) = \int_0^\omega d\omega_1 Q^{r''}(q',\omega_1) Q^{r''}(q'',\omega-\omega_1) . \tag{4.2.7}$$

If now we replace $Q^{r''}$ by the free particle function $Q^{ro''}$, we can perform the integrals analytically. As in Section 3.3.1, here too we use the method suggested by Dubois[61] (see Appendix IV)

to evaluate the integrals. The damping coefficient γ of long wavelength plasmons is given by,

$$\gamma = + \frac{\omega_p}{2q^2} \operatorname{Im} G(q, \omega_p), \qquad (4.2.8)$$

in the $q \to 0$ limit . We have listed in Table (4.1) the value of γ obtained in this way for $r_s = 2$. As seen in the earlier calculations for γ , we notice in this case too that dropping the second term in the expansion of $Q^{r''}(\underset{\sim}{q}, \underset{\sim}{q}', \omega)$ (in equation (4.2.5)), reduces the value of γ by about 70%.

We have investigated the result in the $r_s \to 0$ limit also. If the second term in equation (4.2.5) is dropped, the value of γ in this limit is given by,

$$\gamma \xrightarrow{r_s \to 0} \frac{3\pi}{640} \omega_p^3 [60(1 - \ln 2)] \simeq 0.271 \omega_p^3 \qquad (4.2.9)$$

For comparison we also write the weak coupling perturbation result obtained by Dubois and Kivelson[7],

$$\gamma \longrightarrow \frac{3\pi}{640} \omega_p^3 [34 - 22 \ln 2] \simeq 0.276 \omega_p^3 \qquad (4.2.10)$$

and that obtained by Sharma et al.[59] who used the same approximation as used by us in their mode coupling theory based on Mori formalism [i.e. replace $Q^{r''}$ by $Q^{ro''}$ and then $Q^{ro''}(q-q', \omega-\omega_1)$ by $Q^{ro''}(q', \omega-\omega_1)$],

$$\gamma \longrightarrow \frac{3\pi}{640} \omega_p^3 [63(1 - \ln 2)] \simeq 0.285 \omega_p^3 \qquad (4.2.11)$$

As seen from equations (4.2.9) and (4.2.10), the agreement for γ values in this limit is very good. In case we retain the $\underset{\sim}{q} \cdot \underset{\sim}{\nabla}_{q'} Q^{r''}(q', \omega-\omega_1)$ term in equation (4.2.5), γ in this $r_s \to 0$ limit is also very small :

$$\gamma \rightarrow \frac{3\pi}{640}\,\omega_p^3\,[18(1-\ln 2)] \simeq 0.081\,\omega_p^3 \quad . \qquad (4.2.12)$$

We have also computed γ for r_s varying from 2 to 5 with $Q^{r''}$ replaced by its RPA value. In this case, the t integral is also numerically evaluated . The expression for $\mathrm{Im}G(q,\omega)$ which is then to be evaluated is given by,

$$\mathrm{Im}\,G(q,\omega_p) = +\frac{q}{32\,dr_s}\int_0^\infty dq'\; q'^2 \int_{-1}^{+1} dt\,\{q't + 3qt^2 - 4q't^3\} \int_0^{\omega_p} d\omega_1\; Q^{r''}_{RPA}(q',\omega_1)\; Q^{r''}_{RPA}(q'',\omega-\omega_1), \qquad (4.2.13)$$

where, $q''^2 = q^2 + q'^2 - 2qq't$. The results obtained in this case are also given in Table (4.1). Also listed for comparison are the values of γ calculated in the earlier ad-hoc approximation discussed in Section 3.3.1. The table indicates that the values of γ in the present case are higher than those obtained in the earlier case. The difference in the γ values calculated with $Q^{r''}_{RPA}$ and those obtained using $Q^{ro''}$ is still quite large. This difference is due to the indusion of screening in the former case. In these calculations also, the contributions to γ in the small q limit come from the particle-hole coupling alone. The plasmon-particle-hole and the plasmon-plasmon interactions begin to contribute only for frequencies greater than the plasmon frequency.

As seen from equation (4.2.13), the ω-dependence of $\mathrm{Im}G_1(q,\omega)$ in the small q limit is controlled by a term of the type $Q^{r''}\,Q^{r''}$ i.e. by coupling between the excitation modes

TABLE 4.1

Approximation used		$r_s = 2$	$r_s = 3$	$r_s = 4$	$r_s = 5$
I. Response theory approximation (equation 4.2.13)					
a) $Q''_{RPA}\ Q''_{RPA}$		0.0027	0.0042	0.0055	0.0066
b) $Q^{ro''}\ Q^{ro''}$	computed	0.1813	0.3077	0.4372	0.5761
	analytical	0.1740			
II. Ad-hoc SSTL[1] like approximation (equation 3.3.4)					
a) $Q''_{RPA}\ Q''_{RPA}$		0.0015	0.0023	0.0031	0.0037
$Q^{ro''}\ Q^{ro''}$		0.0919	0.1858	0.2293	0.3215

Contributions to damping coefficient γ in both the approximations - I. Response theory (equation (4.2.13) and II. Ad-hoc SSTL[1] like approximation(equation (3.3.4)).

of the system. Thus, here we have an approximation for $\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$, which is symmetric with respect to interchange of variables $\underset{\sim}{q}$ and $\underset{\sim}{q}'$. Also the mode coupling feature noticed earlier in the ad-hoc approximation is retained here too. Within the approximation made by us (to reduce numerical work) in the small q limit, we see that the value for γ obtained here in the $r_s \to 0$ limit agrees very well with the weak coupling ($r_s \to 0$) perturbation result obtained earlier by Dubois and Kivelson[7]. We note here though that the 70% reduction in the value of γ when the expansion of $Q^{ro''}(q-q',\omega-\omega_1)$ is properly accounted for, should also be present in the calculations of Sharma et al.[59] as well as of Dubois and Kivelson[7].

4.3 EXTRACTION OF $\bar{C}^{(2)}$ FROM THE EQUATION OF MOTION FOR $\bar{f}^{(2)}$

An entirely different approach to obtain $\chi^r(\underset{\sim}{q},\omega)$ and hence the local field $G(\underset{\sim}{q},\omega)$ is based on extracting $\bar{C}^{(2)}$ from the equation of motion for $\bar{f}^{(2)}$. Proceeding in exactly the same manner as for the equation of motion for $\bar{f}^{(1)}$ (Section 3.1), we can obtain an equation of motion for $\bar{f}^{(2)}$. This is given by[8],

$$\left[\hbar\omega - \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q} + \underset{\sim}{k}'\cdot\underset{\sim}{q}')\right] \bar{f}^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$= \frac{1}{V}\Big[\phi_{ext}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\Big\{ f^{(2)eq}_{\underset{\sim}{k}-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}') - f^{(2)eq}_{\underset{\sim}{k}+\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')$$

$$+ f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma'}(\underset{\sim}{q}) - f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'+\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma'}(\underset{\sim}{q})\Big\}\Big]$$

...contd.

$$+\frac{1}{V}\Big[v(\underset{\sim}{q}+\underset{\sim}{q}')\,\bar{n}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\Big\{f^{(2)eq}_{\underset{\sim}{k}-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')-f^{(2)eq}_{\underset{\sim}{k}+\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')$$

$$+f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma'}(\underset{\sim}{q})-f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'+\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma'}(\underset{\sim}{q})\Big\}$$

$$+\sum_{\underset{\sim}{q}''}v(\underset{\sim}{q}'')\sum_{\underset{\sim}{k}''\sigma''}\Big\{\bar{f}^{(3)}_{\underset{\sim}{k}-\underset{\sim}{q}''/2\sigma\,\underset{\sim}{k}'\sigma'\,\underset{\sim}{k}''\sigma''}(\underset{\sim}{q}-\underset{\sim}{q}'',\underset{\sim}{q}',\underset{\sim}{q}'',\omega)-\bar{f}^{(3)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'+\underset{\sim}{q}''/2\sigma'\,\underset{\sim}{k}''\sigma''}(\underset{\sim}{q}-\underset{\sim}{q}'',\underset{\sim}{q}',\underset{\sim}{q}'',\omega)$$

$$+\bar{f}^{(3)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'-\underset{\sim}{q}''/2\sigma'\,\underset{\sim}{k}''\sigma''}(\underset{\sim}{q},\underset{\sim}{q}'-\underset{\sim}{q}'',\underset{\sim}{q}'',\omega)-\bar{f}^{(3)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'+\underset{\sim}{q}''/2\sigma'\,\underset{\sim}{k}''\sigma''}(\underset{\sim}{q},\underset{\sim}{q}'-\underset{\sim}{q}'',\underset{\sim}{q}'',\omega)\Big\}$$

$$+v(\underset{\sim}{q})\Big\{\big(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}-n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\big)\sum_{\underset{\sim}{k}\sigma_1}\bar{f}^{(2)}_{\underset{\sim}{k}\sigma_1\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$+\big(\bar{f}^{(1)}_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)-\bar{f}^{(1)}_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\big)\sum_{\underset{\sim}{k}\sigma_1}f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}\sigma_1}(\underset{\sim}{q})\Big\}+$$

$$+v(\underset{\sim}{q}')\Big\{\big(n_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'}-n_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'}\big)\sum_{\underset{\sim}{k}\sigma_1}\bar{f}^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}\sigma_1}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$+\big(\bar{f}^{(1)}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)-\bar{f}^{(1)}_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\big)\sum_{\underset{\sim}{k}\sigma_1}f^{(2)eq}_{\underset{\sim}{k}\sigma_1\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\Big\}\Big]$$

$$+\frac{1}{V}\Big[\sum_{\underset{\sim}{q}''}v(\underset{\sim}{q}'')\Big\{\bar{f}^{(2)}_{\underset{\sim}{k}-\underset{\sim}{q}''/2\sigma\,\underset{\sim}{k}'+\underset{\sim}{q}''/2\sigma'}(\underset{\sim}{q}-\underset{\sim}{q}'',\underset{\sim}{q}'+\underset{\sim}{q}'',\omega)$$

$$-\bar{f}^{(2)}_{\underset{\sim}{k}+\underset{\sim}{q}''/2\sigma\,\underset{\sim}{k}'-\underset{\sim}{q}''/2\sigma'}(\underset{\sim}{q}-\underset{\sim}{q}'',\underset{\sim}{q}'+\underset{\sim}{q}'',\omega)\Big\}$$

$$+v(\underset{\sim}{q})\Big\{n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\bar{f}^{(1)}_{\underset{\sim}{k}'+\underset{\sim}{q}/2\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)-n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\bar{f}^{(1)}_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\Big\}+$$

$$+v(\underset{\sim}{q}')\Big\{n_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'}\bar{f}^{(1)}_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)-n_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'}\bar{f}^{(1)}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\Big\}\Big] \tag{4.3.1}$$

We note here that the above expression is the correct one although it differs slightly from the corresponding equation obtained by Niklasson[8]. It reduces to the form given by Niklasson only if one makes the additional approximation

$f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) = f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$, which is not true in general ; the correct relation being $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) = f^{(2)eq}_{-k\sigma-k'\sigma'}(q)$ (see Section 4.5).

To give a physical description of the various terms in the right hand side of this equation of motion we assume a classical interpretation of the two particle Wigner distribution function i.e. we assume that $f^{(2)}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t)$ gives the equal time correlation between two particles with moemnta $\hbar k$ and $\hbar k'$. The term in the first square bracket then contains the effect of the external field on each of these particles in the presence of the other. The second term (i.e. the term in the next square bracket), contains the effect of the rest of the particles on each of these particles, again in the presence of the other. The many body effects give rise to the three particle correlation functions $\bar{f}^{(3)}$ present in this term. The mutual interaction between the two particles themselves is contained in the last square bracket.

Aravind et al.[10] retained only the screened effective field terms (i.e. the $\phi_{eff}(q,\omega) = \phi_{ext}(q,\omega) + v(q)\bar{n}(q,\omega)$, terms in the above equation] in the equation of motion for $\bar{f}^{(2)}$ obtained by Niklasson[8] (which is obtained by making the additional approximation $f^{(2)eq}_{k\sigma k'\sigma'}(-q) = f^{(2)eq}_{-k\sigma-k'\sigma'}(q)$) and substituted the resulting $\bar{f}^{(2)}$ into the equation of motion for $\bar{f}^{(1)}_{k\sigma}(q,\omega)$ to obtain $\chi^r(\underset{\sim}{q},\omega)$ as,

$$\chi^r(\underset{\sim}{q},\omega) = \frac{\chi^{r0}(\underset{\sim}{q},\omega) + \chi^{(1)}(\underset{\sim}{q},\omega)}{1 - v(q)\{\chi^{r0}(\underset{\sim}{q},\omega) + \chi^{(1)}(\underset{\sim}{q},\omega)\}}, \qquad (4.3.2)$$

where,

$$\chi^{(1)}(\underset{\sim}{q},\omega) = \frac{1}{V^2}\sum_{\underset{\sim}{q}'} v(q') \sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} \Big[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}') \cdot$$

$$\Big[D_2^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}}{2}, \underset{\sim}{k}'; q-q', q'\right)\Big\{ D_1^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}, q, \omega\right) - D_1^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\right)\Big\}$$

$$+ D_2^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}}{2}, \underset{\sim}{k}'; \underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}'\right)\Big\{ D_1^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\right) - D_1^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\right)\Big\}\Big]$$

$$+ f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}'+\underset{\sim}{q}) \Big\{ D_1^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\right) + D_1^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2}, \underset{\sim}{q}, \omega\right)\Big\}$$

$$\cdot\Big\{ D_2^{-1}\left(\underset{\sim}{k}, \underset{\sim}{k}'+\frac{\underset{\sim}{q}}{2}; \underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}'\right) - D_2^{-1}\left(\underset{\sim}{k}, \underset{\sim}{k}'-\frac{\underset{\sim}{q}}{2}; \underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}'\right)\Big\}\Big] . \qquad (4.3.3)$$

Here,

$$D_2(\underset{\sim}{k}, \underset{\sim}{k}'; \underset{\sim}{q}, \underset{\sim}{q}') = \hbar\omega + i\delta - \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q} + \underset{\sim}{k}'\cdot\underset{\sim}{q}') . \qquad (4.3.4)$$

From (4.3.2) and (4.1.33), the local field $G(q,\omega)$ was then extracted.

We now use a similar approximation as the one used by Aravind et al.[10], to construct $\bar{C}^{(2)}$ instead, i.e., we use

$$\bar{C}^{(2)}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) = \sum_{\substack{\underset{\sim}{k}\sigma \\ \underset{\sim}{k}'\sigma'}} \bar{f}^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) . \qquad (4.3.5)$$

From the $\bar{C}^{(2)}$ thus obtained we have,

$$\frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\, \bar{C}^{(2)}(\underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}', \omega)\, \chi^{r0}(\underset{\sim}{q}, \underset{\sim}{q}', \omega)$$

$$= \frac{1}{nV^2}\left\{ \phi_{ext}(\underset{\sim}{q}, \omega) + v(\underset{\sim}{q})\, \bar{n}(\underset{\sim}{q}, \omega)\right\} \sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}') \sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} D_2^{-1}(\underset{\sim}{k}, \underset{\sim}{k}'; \underset{\sim}{q}-\underset{\sim}{q}', \underset{\sim}{q}')$$

$$\cdot\Big\{ f^{(2)eq}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}') - f^{(2)eq}_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}') + f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}(\underset{\sim}{q}-\underset{\sim}{q}')$$

$$- f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'+\underset{\sim}{q}/2\sigma'}(\underset{\sim}{q}-\underset{\sim}{q}')\Big\}\, \chi^{r0}(\underset{\sim}{q}, \underset{\sim}{q}', \omega) ,$$

$$= \frac{1}{nV^2}\{\phi_{ext}(\underset{\sim}{q},\omega) + v(\underset{\sim}{q})\bar{n}(\underset{\sim}{q},\omega)\}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$\sum_{\substack{\underset{\sim}{k}\sigma \\ \underset{\sim}{k}'\sigma'}}\Big[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')\{D_2^{-1}(\underset{\sim}{k}+\tfrac{\underset{\sim}{q}}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}') - D_2^{-1}(\underset{\sim}{k}-\tfrac{\underset{\sim}{q}}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}')\}$$

$$+ f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}-\underset{\sim}{q}')\{D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}'+\tfrac{\underset{\sim}{q}}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}') - D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}'-\tfrac{\underset{\sim}{q}}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}')\}\Big], \qquad (4.3.5)$$

$$= \{\phi_{ext}(\underset{\sim}{q},\omega) + v(\underset{\sim}{q})\,\bar{n}(\underset{\sim}{q},\omega)\}\,\chi^{1}(\underset{\sim}{q},\omega), \qquad (4.3.6)$$

where,
$$D_2(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}') = \hbar\omega + i\delta - (\hbar/m)(\underset{\sim}{k}\cdot\underset{\sim}{q} + \underset{\sim}{k}'\cdot\underset{\sim}{q}') \qquad (4.3.7)$$

Substituting above term into equation (3.1.9) and using the relation (2.1.7), between $\bar{n}(\underset{\sim}{q},\omega)$ and $\chi^{r}(\underset{\sim}{q},\omega)$, we obtain,

$$\chi^{r}(\underset{\sim}{q},\omega) = \frac{\chi^{r0}(\underset{\sim}{q},\omega) + \chi^{1}(\underset{\sim}{q},\omega)}{1 - v(q)\{\chi^{r0}(\underset{\sim}{q},\omega) + \chi^{1}(\underset{\sim}{q},\omega)\} - \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\{S(\underset{\sim}{q}-\underset{\sim}{q}')-1\}\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega)}, \qquad (4.3.8)$$

where $\chi^{1}(\underset{\sim}{q},\omega)$ is defined above in equation (4.3.6)

If in equation (4.3.5), we use the diagonal approximation for $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$, i.e. we write,

$$\sum_{\underset{\sim}{k}'\sigma'} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = \delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k}\underset{\sim}{k}'}\sum_{\underset{\sim}{k}_2\sigma_2} f^{(2)}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}_2\sigma_2}(\underset{\sim}{q}), \qquad (4.3.9)$$

the expression for $\chi^{1}(q,\omega)$ reduces to,

$$\chi^{1}_{d}(\underset{\sim}{q},\omega) = \frac{1}{nV^2}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\cdot$$

$$\Big[\sum_{\underset{\sim}{k}\sigma}\{D_1^{-1}(\underset{\sim}{k}+\tfrac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega) - D_1^{-1}(\underset{\sim}{k}-\tfrac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega)\}\sum_{\underset{\sim}{k}_2\sigma_2} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}_2\sigma_2}(-\underset{\sim}{q}')$$

$$+ \sum_{\underset{\sim}{k}\sigma}\{D_1^{-1}(\underset{\sim}{k}+\tfrac{\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega) - D_1^{-1}(\underset{\sim}{k}-\tfrac{\underset{\sim}{q}'}{2},\underset{\sim}{q},\omega)\}\sum_{\underset{\sim}{k}_2\sigma_2} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}_2\sigma_2}(\underset{\sim}{q}-\underset{\sim}{q}')\Big] \qquad (4.3.10)$$

which is the same as $\chi^{A0}(q,\omega)$ obtained in Section 4.1 using an entirely different approach (see equation (4.1.28)). If

in tnis equation we use the Hartree Fock expression for $f^{(2)eq}$ (i.e. if we use the equilibrium two particle function calculated for the non-interacting system), given by,

$$\left[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}') \right]^{HF} = -\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\,\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{q}+\underset{\sim}{q}',0}\,n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\,n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}, \tag{4.3.11}$$

both $\chi^{A0}(\underset{\sim}{q},\omega)$ and $\chi^{1}(\underset{\sim}{q},\omega)$ reduce to,

$$\chi^{1}_{HF}(\underset{\sim}{q},\omega) = \frac{1}{nV^2}\sum_{\underset{\sim}{q}'}\left\{v(q')\,\chi^{x0}(\underset{\sim}{q},\underset{\sim}{q}',\omega) + v(\underset{\sim}{q}-\underset{\sim}{q}')\,\chi^{x0}(\underset{\sim}{q},\underset{\sim}{q}-\underset{\sim}{q}',\omega)\right\}$$

$$\cdot \sum_{\underset{\sim}{k}\sigma}\left\{\tilde{D}_1^{-1}(\underset{\sim}{k}+\frac{\underset{\sim}{q}}{2},\underset{\sim}{q},\omega) - \tilde{D}_1^{-1}(\underset{\sim}{k}-\frac{\underset{\sim}{q}}{2},\underset{\sim}{q},\omega)\right\} n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\,n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\,. \tag{4.3.12}$$

This is the same result as obtained by Aravind et al[10] in the small q limit when they too used the Hartee Fock expression for $f^{(2)eq}$. The $\chi^{A1}(\underset{\sim}{q},\omega)$ present in our approach will definitely give an improvement over $\chi^{A0}(\underset{\sim}{q},\omega)$ due to the presence of $F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$. The present theory thus goes beyond other equation of motion approaches in including higher order correlations. The mode coupling feature observed could be a result of the inclusion of these higher order correlations.

We also note that in the limit of $q \to 0$ or $q/w \to 0$, both $\chi^{(1)}(q,\omega)$, given by (4.3.4) as used by Aravind et al.[10] and $\chi^{1}_{d}(q,\omega)$ given by (4.3.7) as derived here (or $\chi^{A0}(q,\omega)$ given by (4.1.28) derived in Section 4.1) will go to the same limiting form except for the imaginary part because of the diagonal - type approximation (4.3.9) made here. This would mean that the long wavelength plasmon dispersion would essentially be the same for the two cases, although the plasmon

damping coefficient will differ. However, to obtain the plasmon damping, Aravind et al. used ansätze for $f^{(2)eq}$ which are very differrnt from the RPA form as derived in a later section and without undertaking heavy computational work, we are unable to verify if the damping coefficient obtained by Aravind et al. is really meaningful or not.

We finally note here that in the right hand side of the two particle equation of motion, in addition to the terms retained in the approximation used by Aravind et al.[10], if we replace the $\bar{f}^{(1)}$ terms by their RPA expression, i.e.,

$$\bar{f}^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega) = \{\phi_{ext}(\underset{\sim}{q},\omega) + v(\underset{\sim}{q})\bar{n}(\underset{\sim}{q},\omega)\}\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega), \qquad (4.3.13)$$

and construct $\bar{C}^{(2)}$ from the resultant $\bar{f}^{(2)}$, we get (proceeding in exactly the same manner as described above),

$$\chi^{r}(q,\omega) = \frac{\chi^{r0}(\underset{\sim}{q},\omega) + \chi^{(2)}(\underset{\sim}{q},\omega)}{1 - v(q)\{\chi^{r0}(q,\omega) + \chi^{(2)}(q,\omega)\} - \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\{S(\underset{\sim}{q}-\underset{\sim}{q}') - 1\}\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega)}, \qquad (4.3.14)$$

where,

$$\chi^{(2)}(\underset{\sim}{q},\omega) = \frac{1}{nV^2}\sum_{\underset{\sim}{q}'} v(\underset{\sim}{q}')\,\chi^{r0}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}$$

$$\Big[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}-\underset{\sim}{q}')\Big\{\bar{D}_2^{-1}\Big(\underset{\sim}{k},\underset{\sim}{k}'+\frac{\underset{\sim}{q}}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big) - \bar{D}_2^{-1}\Big(\underset{\sim}{k},\underset{\sim}{k}'-\frac{\underset{\sim}{q}}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big)\Big\}$$

$$+ f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')\Big\{\bar{D}_2^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big) - \bar{D}_2^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big)\Big\}$$

... Contd.

$$+ v(\underset{\sim}{q}-\underset{\sim}{q}') \sum_{\underset{\sim}{k},\sigma_1} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}\sigma_1}(\underset{\sim}{q}-\underset{\sim}{q}')\left\{\bar{D}_2^{-1}\left(\underset{\sim}{k},\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)-\bar{D}_2^{-1}\left(\underset{\sim}{k},\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)\right\}$$

$$\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$$

$$+ v(\underset{\sim}{q}') \sum_{\underset{\sim}{k},\sigma_1} f^{(2)eq}_{\underset{\sim}{k},\sigma_1\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')\left\{\bar{D}_2^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)-\bar{D}_2^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)\right\}$$

$$\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)$$

$$+ v(\underset{\sim}{q}-\underset{\sim}{q}')\, n_{\underset{\sim}{k}\sigma}\left\{\bar{D}_2^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};\underset{\sim}{k}-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)-\bar{D}_2^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2},\underset{\sim}{k}'+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)\right\}$$

$$\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$$

$$+ v(\underset{\sim}{q}')\, n_{\underset{\sim}{k}'\sigma'}\left\{\bar{D}_2^{-1}\left(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2},\underset{\sim}{k}'-\frac{\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)-\bar{D}_2^{-1}\left(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2},\underset{\sim}{k}'-\frac{\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\right)\right\}$$

$$\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\Big] \qquad (4.3.15)$$

The inclusion of $\bar{f}^{(1)}$ terms incorporates the self energy of the electrons in the system. For example, if we substitute the $\bar{f}^{(2)}$ obtained above into the equation of motion for $\bar{f}^{(1)}$, we would get an integral equation for $\bar{f}^{(1)}$ whose solution would contain a self energy term. In the next section we have obtained the above result using response theory.

4.4 EXPRESSION FOR $\bar{D}^{(2)}$ USING RESPONSE THEORY

Here we describe yet another approach to obtain $\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ and hence the density-density response function $\chi^{r}(\underset{\sim}{q},\omega)$. We start with defining a response function $K(\underset{\sim}{r},\underset{\sim}{r}',t)$ corresponding to $\bar{D}^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ in the presence of an external field $\phi_{ext}(\underset{\sim}{r},t)$. Since we are interested in deviation from equilibrium values to linear order in the external potential, we can use linear response theory to write

the following expression :

$$\bar{D}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', t) = \int_{-\infty}^{\infty} dt' \, d\underset{\sim}{r}'' \, K(\underset{\sim}{r}-\underset{\sim}{r}'', \underset{\sim}{r}'-\underset{\sim}{r}'', t-t') \, \Phi_{ext}(\underset{\sim}{r}'', t') \, . \tag{4.4.1}$$

Here we have made use of the fact that the system has translational invariance. The response function $K(\underset{\sim}{r}-\underset{\sim}{r}'', \underset{\sim}{r}'-\underset{\sim}{r}''; t-t')$ can then be written as,

$$K(\underset{\sim}{r}-\underset{\sim}{r}'', \underset{\sim}{r}'-\underset{\sim}{r}''; t-t') = \frac{\theta(t-t')}{i\hbar} \left\langle \left[\hat{\hat{\rho}}(\underset{\sim}{r}-\underset{\sim}{r}'', t-t') \, \hat{\hat{\rho}}(\underset{\sim}{r}'-\underset{\sim}{r}'', t-t') \, , \, \hat{\rho}(0,0) \right]_- \right\rangle_{eq} \tag{4.4.2}$$

Taking the space Fourier transform we then have in Fourier space,

$$\bar{D}^{(2)}(\underset{\sim}{q}, \underset{\sim}{q}', t) = K(\underset{\sim}{q}, \underset{\sim}{q}', t) \, \Phi_{ext}(\underset{\sim}{q}+\underset{\sim}{q}', t) \, , \tag{4.4.3}$$

where the Fourier transform of K is given by,

$$K(\underset{\sim}{q}, \underset{\sim}{q}', t) = \frac{\theta(t)}{i\hbar} \left\langle \left[\hat{\hat{\rho}}(\underset{\sim}{q}, t) \, \hat{\hat{\rho}}(\underset{\sim}{q}', t) \, , \, \hat{\rho}(-\underset{\sim}{q}-\underset{\sim}{q}') \right]_- \right\rangle_{eq} \tag{4.4.4}$$

We define another function $K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}, \underset{\sim}{q}'; t)$, where,

$$K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}, \underset{\sim}{q}', t) = \frac{\theta(t)}{i\hbar} \left\langle \left[\hat{\hat{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) \, \hat{\hat{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \, , \, \hat{\rho}(-q-q', 0) \right]_- \right\rangle_{eq} \tag{4.4.5}$$

which is such that,

$$K(\underset{\sim}{q}, \underset{\sim}{q}', t) = \sum_{\underset{\sim}{k}\sigma \, \underset{\sim}{k}'\sigma'} K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}, \underset{\sim}{q}', t) \, . \tag{4.4.6}$$

The time derivative of $K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}, \underset{\sim}{q}', t)$ is then given by,

$$\begin{aligned} i\hbar \frac{\partial}{\partial t} K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}, \underset{\sim}{q}', t) &= \frac{\delta(t)}{V} \left\langle \left[\hat{\hat{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) \, \hat{\hat{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \, , \, \hat{\rho}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \right]_- \right\rangle_{eq} \\ &+ \frac{\theta(t)}{V} \left\langle \left[\frac{\partial \hat{\hat{\rho}}}{\partial t}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) \, \hat{\hat{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \, , \, \hat{\rho}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \right]_- \right\rangle_{eq} \\ &+ \frac{\theta(t)}{V} \left\langle \left[\hat{\hat{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, t) \, \frac{\partial}{\partial t} \hat{\hat{\rho}}_{\underset{\sim}{k}'\sigma}(\underset{\sim}{q}', t) \, , \, \hat{\rho}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \right]_- \right\rangle_{eq} . \end{aligned} \tag{4.4.7}$$

The Hamiltonian of the system in equilibrium (i.e., in the absence of an external field), when written in terms of the density operators is given by, (see Appendix II, equation (A.2.2).

$$H(t) = \sum_{\underset{\sim}{k},\sigma_1} \frac{\hbar^2 k_1^2}{2m} \hat{\rho}_{\underset{\sim}{k}_1\sigma_1}(0,0) + \frac{1}{2V}\sum_{\underset{\sim}{q}_1} v(\underset{\sim}{q}_1)\left[\hat{\rho}(\underset{\sim}{q}_1,t)\hat{\rho}(-\underset{\sim}{q}_1,t) - N\right]. \quad (A.4.8)$$

Hence the equation of motion for $\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$ in the absence of an external potential is,

$$i\hbar \frac{\partial}{\partial t}\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$$

$$+ \frac{1}{2V}\sum_{\underset{\sim}{q}_1} v(\underset{\sim}{q}_1)\Big[\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\left\{\hat{\rho}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t) - \hat{\rho}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\right\}$$

$$+\left\{\hat{\rho}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t) - \hat{\rho}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\right\}\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\Big], \quad (4.4.9)$$

where we have used simple commutator properties and the result (A.6.3) from Appendix VI, i.e.,

$$\left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}),\ \hat{\rho}(\underset{\sim}{q}')\right]_- = \left\{\hat{\rho}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}') - \hat{\rho}_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}')\right\}. \quad (4.4.10)$$

Equation (4.4.9) can also be written as,

$$i\hbar \frac{\partial}{\partial t}\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$$

$$+ \frac{v(\underset{\sim}{q})}{V}\left(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\right)\hat{\tilde{\rho}}(\underset{\sim}{q},t)$$

$$+\frac{1}{2V}\sum_{\underset{\sim}{q}_1} v(\underset{\sim}{q}_1)\Big[\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\left\{\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t) - \hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\right\}$$

$$+\left\{\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t) - \hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\right\}\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\Big]. \quad (4.4.11)$$

Using the above equation of motion for $\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$ and the definition of $K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t)$, we can then write,

$$\frac{\Theta(t)}{V}\left\langle\left[\frac{\partial\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)}{\partial t}\;\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

$$=\frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})K_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t)$$

$$+\frac{v(q)}{V}(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}-n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\sum_{\underset{\sim}{k}_1\sigma_1}K_{\underset{\sim}{k}_1\sigma_1,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t)$$

$$+\frac{1}{2V}\sum_{\underset{\sim}{q}_1}v(q_1)\Bigg[\frac{\Theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

$$+\frac{\Theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

$$-\frac{\Theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

$$-\frac{\Theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}(\underset{\sim}{q}_1,t)\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

(4.4.12)

We evaluate the equilibrium values of the commutators by decoupling a commutator as,

$$\langle[ABC,D]_-\rangle_{eq}=\langle AB\rangle_{eq}\langle[C,D]_-\rangle_{eq}$$

$$+\langle AC\rangle_{eq}\langle[B,D]_-\rangle_{eq}+\langle BC\rangle_{eq}\langle[A,D]_-\rangle_{eq}\;. \qquad (4.4.13)$$

Decoupling in this way and using the definitions of $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t)$, given by,

$$\chi^{v}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t)=\frac{\Theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t),\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},0)\right]_-\right\rangle_{eq}, \qquad (4.4.14)$$

we can write,

$$\frac{\theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\delta}}(\underset{\sim}{q}_1,t)\hat{\tilde{\delta}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\ \hat{\tilde{\delta}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

$$= \delta_{\underset{\sim}{q},0}\left\langle\hat{\tilde{\delta}}(\underset{\sim}{q}_1,t)\hat{\tilde{\delta}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1,t)\right\rangle_{eq}\sum_{\underset{\sim}{k}_1\sigma_1}\chi^r_{\underset{\sim}{k}_1\sigma_1,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t)$$

$$+\ \delta_{\underset{\sim}{q}_1+\underset{\sim}{q}',0}\left\langle\hat{\tilde{\delta}}(\underset{\sim}{q}_1,t)\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t)\right\rangle_{eq}\sum_{\underset{\sim}{k}_1\sigma_1}\chi^r_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}+\underset{\sim}{q}',t)$$

$$+\ \delta_{\underset{\sim}{q}_1,\underset{\sim}{q}+\underset{\sim}{q}'}\left\langle\hat{\tilde{\delta}}_{\underset{\sim}{k}-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma}(-\underset{\sim}{q}',t)\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t)\right\rangle_{eq}\chi^r(\underset{\sim}{q}+\underset{\sim}{q}',t)\ . \qquad (4.4.15)$$

The detailed steps are given in Appendix VI. Also listed in the Appendix are the results for the other commutators (equations (A.6 .6) to (A.6.8). Using all of these,

$$\frac{\theta(t)}{V}\left\langle\left[\frac{\partial\hat{\tilde{\delta}}}{\partial t}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t),\ \hat{\tilde{\delta}}(-\underset{\sim}{q}-\underset{\sim}{q}',0)\right]_-\right\rangle_{eq}$$

$$= \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})K_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t)$$

$$+\ \frac{v(\underset{\sim}{q})}{V}(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}-n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\sum_{\underset{\sim}{k}_1\sigma_1}K_{\underset{\sim}{k}_1\sigma_1,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',t)$$

$$+\ \frac{v(\underset{\sim}{q}+\underset{\sim}{q}')}{V}\chi^r(\underset{\sim}{q}+\underset{\sim}{q}',t)\left[\left\langle\hat{\tilde{\delta}}_{\underset{\sim}{k}-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma}(-\underset{\sim}{q}')\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}')\right\rangle_{eq}-\left\langle\hat{\tilde{\delta}}_{\underset{\sim}{k}+\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}\sigma}(-\underset{\sim}{q}')\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}')\right\rangle_{eq}\right]$$

$$+\ \frac{v(\underset{\sim}{q}')}{V}\left\langle\hat{\tilde{\delta}}(-\underset{\sim}{q}')\hat{\tilde{\delta}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}')\right\rangle_{eq}\sum_{\underset{\sim}{k}_1\sigma_1}\left\{\chi^r_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}+\underset{\sim}{q}',t)-\chi^r_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}+\underset{\sim}{q}',t)\right\}$$

$$+\ \delta_{\underset{\sim}{q},0}\frac{1}{2V}\sum_{\underset{\sim}{q}_1}v(\underset{\sim}{q}_1)\left[\left\langle\hat{\tilde{\delta}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\hat{\tilde{\delta}}(\underset{\sim}{q}_1)\right\rangle_{eq}+\left\langle\hat{\tilde{\delta}}(\underset{\sim}{q}_1)\hat{\tilde{\delta}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\right\rangle_{eq}\right.$$

$$\left.-\left\langle\hat{\tilde{\delta}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\hat{\tilde{\delta}}(\underset{\sim}{q}_1)\right\rangle_{eq}-\left\langle\hat{\tilde{\delta}}(\underset{\sim}{q}_1)\hat{\tilde{\delta}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\right\rangle_{eq}\right]\sum_{\underset{\sim}{k}_1\sigma_1}\chi^r_{\underset{\sim}{k}'\sigma'\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}',t).$$

(4.4.16)

Proceeding in a similar manner we can obtain an expression for the third term in the right hand side of equation (4.4.7) i.e. for $\frac{\theta(t)}{V} \left\langle \left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) \frac{\partial \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',t)}{\partial t}, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0) \right]_- \right\rangle_{eq}$.

Similarly using equation (4.4.10), we can write,

$$\left\langle \left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},0) \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',0), \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}',0) \right]_- \right\rangle_{eq}$$

$$= \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},0) \hat{\tilde{\rho}}_{\underset{\sim}{k}'-\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}\sigma'}(-\underset{\sim}{q},0) \right\rangle_{eq} - \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},0) \hat{\tilde{\rho}}_{\underset{\sim}{k}'+\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}\sigma'}(-\underset{\sim}{q},0) \right\rangle_{eq}$$

$$+ \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma}(-\underset{\sim}{q}',0) \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',0) \right\rangle_{eq} - \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}+\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}\sigma}(-\underset{\sim}{q}',0) \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',0) \right\rangle_{eq} \quad (4.4.17)$$

Substituting results from equations (4.4.16), (4.4.17) etc., into equation (.4.4.7), and taking the Fourier transform with respect to time we have,

$$K_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \left[1 + v(\underset{\sim}{q}+\underset{\sim}{q}')\chi'(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\right] \frac{1}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')$$

$$\cdot \left[\left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) \hat{\tilde{\rho}}_{\underset{\sim}{k}'-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma'}(-\underset{\sim}{q}) \right\rangle_{eq} - \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) \hat{\tilde{\rho}}_{\underset{\sim}{k}'+\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma'}(-\underset{\sim}{q}) \right\rangle_{eq} \right.$$

$$\left. + \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}-\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma}(-\underset{\sim}{q}') \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \right\rangle_{eq} - \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}+\frac{(\underset{\sim}{q}+\underset{\sim}{q}')}{2}\sigma}(-\underset{\sim}{q}') \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \right\rangle_{eq} \right]$$

... Contd.

$$+\frac{v(q)}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}-n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\sum_{\underset{\sim}{k}_1\sigma_1} K_{\underset{\sim}{k}_1\sigma_1,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$+\frac{v(q')}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')(n_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'}-n_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'})\sum_{\underset{\sim}{k}_1\sigma_1} K_{\underset{\sim}{k}\sigma,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$+\frac{v(q)}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\hat{\tilde{\rho}}(-\underset{\sim}{q})\rangle_{eq}$$

$$\sum_{\underset{\sim}{k}_1\sigma_1}\{\chi^r_{\underset{\sim}{k}'+\underset{\sim}{q}/2\sigma',\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)-\chi^r_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma',\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\}$$

$$+\frac{v(q')}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')\langle\hat{\tilde{\rho}}(-\underset{\sim}{q}')\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(q')\rangle_{eq}$$

$$\sum_{\underset{\sim}{k}_1\sigma_1}\{\chi^r_{\underset{\sim}{k}_1\sigma_1,\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)-\chi^r_{\underset{\sim}{k}_1\sigma_1,\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\}$$

$$+\frac{1}{2V}\sum_{q_1} v(\underset{\sim}{q}_1)\Big[\delta_{\underset{\sim}{q},0}\, D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')\{\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\rangle_{eq}$$

$$+\langle\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\rangle_{eq}-\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\rangle_{eq}$$

$$-\langle\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\rangle_{eq}\}\sum_{\underset{\sim}{k}_1\sigma_1}\chi^r_{\underset{\sim}{k}'\sigma',\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}',\omega)$$

$$+\delta_{\underset{\sim}{q}',0}\, D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')\{\langle\hat{\tilde{\rho}}(q_1)\hat{\tilde{\rho}}_{\underset{\sim}{k}'-\underset{\sim}{q}_1/2\sigma'}(-q_1)\rangle_{eq}+\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}'-\underset{\sim}{q}_1/2\sigma'}(-q_1)\hat{\tilde{\rho}}(q_1)\rangle_{eq}$$

$$-\langle\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\hat{\tilde{\rho}}_{\underset{\sim}{k}'+\underset{\sim}{q}_1/2\sigma'}(-\underset{\sim}{q}_1)\rangle_{eq}-\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}'+\underset{\sim}{q}_1/2\sigma'}(-\underset{\sim}{q}_1)\hat{\tilde{\rho}}(q_1)\rangle_{eq}\}\sum_{\underset{\sim}{k}_1\sigma_1}\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q},\omega)\Big]$$

(4.4.18)

As the quantities $\langle\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\rangle_{eq}$, etc. are real,

$$\langle\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\rangle_{eq}=\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1)\hat{\tilde{\rho}}(\underset{\sim}{q}_1)\rangle_{eq}.$$

Then, with simple algebraic manipulations we can show that in the last term in the square brackets in equation (4,4.18), the terms cancel each other. We assume that in the above equation $\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ is given by its RPA form, i.e.,

$$\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\left[\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k}\underset{\sim}{k}'} + \frac{v(q)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)}{\epsilon^{r}(\underset{\sim}{q},\omega)}\right],$$

$$= \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\left[\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k}\underset{\sim}{k}'} + v(q)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) + v^{2}(q)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(q,\omega)\,\chi^{r0}(\underset{\sim}{q},\omega)\right]. \tag{4.4.19}$$

Here,

$$\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega) = \frac{1}{\pi V}\,\frac{n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}}{\omega + i\delta - (\pi/m)(\underset{\sim}{k}\cdot\underset{\sim}{q})} \tag{4.4.20}$$

and we have used the RPA expression for $1/\epsilon^{r}(\underset{\sim}{q},\omega)$.

Equation (4.4.19) gives,

$$\sum_{\underset{\sim}{k}_1\sigma_1} \chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\left[1 + v(q)\,\chi^{r}(\underset{\sim}{q},\omega)\right], \tag{4.4.21a}$$

and

$$\sum_{\underset{\sim}{k}_1\sigma_1} \chi^{r}_{\underset{\sim}{k}_1\sigma_1\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\left[1 + v(q)\,\chi^{r}(\underset{\sim}{q},\omega)\right]. \tag{4.4.21b}$$

We define another function $K^{eff}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega')$ via the relation,

$$K_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = K^{eff}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)\left\{1 + v(\underset{\sim}{q}+\underset{\sim}{q}')\chi^{r}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\right\}, \tag{4.4.22a}$$

so that,

$$K(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \left\{1 + v(\underset{\sim}{q}+\underset{\sim}{q}')\chi^{r}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\right\} K^{eff}(\underset{\sim}{q},\underset{\sim}{q}',\omega), \tag{4.4.22b}$$

where,

$$K^{eff}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} K^{eff}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega). \tag{4.4.22c}$$

Using equations (4.4.21) in equation (4.4.18) for $K_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ we get,

$$K^{eff}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \bar{K}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$$

$$+ v(\underset{\sim}{q}) \sum_{\underset{\sim}{k}_1\sigma_1} \chi^{r0}_{\underset{\sim}{k}\sigma}\left(\underset{\sim}{q},\ \omega - \frac{\pi}{m}\,\underset{\sim}{k}_1\cdot\underset{\sim}{q}'\right) \cdot N_{\underset{\sim}{k}_1\sigma_1}$$

$$+ v(\underset{\sim}{q}') \sum_{\underset{\sim}{k}_1\sigma_1} \chi^{r0}_{\underset{\sim}{k}_1\sigma_1}\left(\underset{\sim}{q}',\ \omega - \frac{\pi}{m}\,\underset{\sim}{k}\cdot\underset{\sim}{q}\right) M_{\underset{\sim}{k}\sigma}, \tag{4.4.23}$$

where,

$$\bar{K}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \frac{1}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}')$$

$$\Big[\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) \hat{\tilde{\rho}}_{\underset{\sim}{k}'-(\underset{\sim}{q}+\underset{\sim}{q}')/2\,\sigma'}(-\underset{\sim}{q}) \rangle_{eq} - \langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) \hat{\tilde{\rho}}_{\underset{\sim}{k}'+(\underset{\sim}{q}+\underset{\sim}{q}')/2\,\sigma'}(-\underset{\sim}{q}) \rangle_{eq}$$

$$+ \langle \hat{\tilde{\rho}}_{\underset{\sim}{k}-(\underset{\sim}{q}+\underset{\sim}{q}')/2\,\sigma}(-\underset{\sim}{q}') \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \rangle_{eq} - \langle \hat{\tilde{\rho}}_{\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{q}')/2\,\sigma}(-\underset{\sim}{q}') \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \rangle_{eq} \Big]$$

$$+ \frac{v(q)}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}') \langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) \hat{\tilde{\rho}}(-\underset{\sim}{q}) \rangle_{eq}$$

$$\Big\{ \chi^{ro}_{\underset{\sim}{k}'+\underset{\sim}{q}/2\,\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) - \chi^{ro}_{\underset{\sim}{k}'-\underset{\sim}{q}/2\,\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) \Big\}$$

$$+ \frac{v(q')}{V} D_2^{-1}(\underset{\sim}{k},\underset{\sim}{k}';\underset{\sim}{q},\underset{\sim}{q}') \langle \hat{\tilde{\rho}}(-\underset{\sim}{q}') \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \rangle_{eq}$$

$$\cdot \Big\{ \chi^{ro}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\,\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) - \chi^{ro}_{\underset{\sim}{k}-\underset{\sim}{q}'/2\,\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) \Big\} \quad ; \quad (4.4.24)$$

$$N_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \sum_{\underset{\sim}{k},\sigma} K^{eff}_{\underset{\sim}{k},\sigma,\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega) \quad ; \quad (4.4.25)$$

and

$$M_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \sum_{\underset{\sim}{k},\sigma} K^{eff}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k},\sigma}(\underset{\sim}{q},\underset{\sim}{q}',\omega) . \quad (4.4.26)$$

If we approximate,

$$\chi^{ro}_{\underset{\sim}{k}\sigma}\left(\underset{\sim}{q},\ \omega - \frac{\hbar}{m}(\underset{\sim}{k}'.\underset{\sim}{q}')\right) \simeq \chi^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega) , \quad (4.4.27a)$$

$$\chi^{ro}_{\underset{\sim}{k}'\sigma'}\left(\underset{\sim}{q}',\ \omega - \frac{\hbar}{m}(\underset{\sim}{k}.\underset{\sim}{q})\right) \simeq \chi^{ro}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',\omega) , \quad (4.4.27b)$$

then we obtain a simple equation for $K^{eff}(\underset{\sim}{q},\omega)$ from equation (4.4.23),

$$K^{eff}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \frac{\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} \bar{K}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)}{1-\{v(q)\chi^{ro}(\underset{\sim}{q},\omega) + v(q')\chi^{ro}(\underset{\sim}{q}',\omega)\}} . \quad (4.4.28)$$

$\bar{K}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ can be written in a more simplified manner by

writing it in terms of the equilibrium two particle function. By definition,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(q) = \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-q) \right\rangle_{eq} - \delta_{\sigma\sigma'}\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\, n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}. \qquad (4.4.29)$$

Using this and making some simple algebraic manipulations to obtain a symmetric form for $\bar{K}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$, we finally obtain,

$$\begin{aligned}
\bar{K}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = {} & \frac{1}{V}\sum_{\substack{\underset{\sim}{k}\sigma\\ \underset{\sim}{k}'\sigma'}} \Big[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) \Big\{ D_2^{-1}\Big(\underset{\sim}{k}, \underset{\sim}{k}' + \frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}; \underset{\sim}{q},\underset{\sim}{q}'\Big) - D_2^{-1}\Big(\underset{\sim}{k}, \underset{\sim}{k}' - \frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}; \underset{\sim}{q},\underset{\sim}{q}'\Big)\Big\} \\
& + f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')\Big\{ D_2^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}, \underset{\sim}{k}'; \underset{\sim}{q},\underset{\sim}{q}'\Big) - D_2^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}+\underset{\sim}{q}'}{2}, \underset{\sim}{k}'; \underset{\sim}{q},\underset{\sim}{q}'\Big)\Big\} \\
& + v(\underset{\sim}{q}) \sum_{\underset{\sim}{k}_1\sigma_1} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q})\Big\{ D_2^{-1}\Big(\underset{\sim}{k}, \underset{\sim}{k}' - \frac{\underset{\sim}{q}}{2}; q, q'\Big) - D_2^{-1}\Big(\underset{\sim}{k}, \underset{\sim}{k}' + \frac{\underset{\sim}{q}}{2}; \underset{\sim}{q},\underset{\sim}{q}'\Big)\Big\} \chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) \\
& + v(\underset{\sim}{q}') \sum_{\underset{\sim}{k}_1\sigma_1} f^{(2)eq}_{\underset{\sim}{k}_1\sigma_1\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}')\Big\{ D_2^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2}, \underset{\sim}{k}'; q, q'\Big) - D_2^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2}, \underset{\sim}{k}'; \underset{\sim}{q},\underset{\sim}{q}'\Big)\Big\} \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) \\
& + v(\underset{\sim}{q})\, n_{\underset{\sim}{k}\sigma}\Big\{ D_2^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}}{2}, \underset{\sim}{k}'-\frac{\underset{\sim}{q}}{2}; q, q'\Big) - D_2^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}}{2}, \underset{\sim}{k}'+\frac{\underset{\sim}{q}}{2}; q, q'\Big)\Big\} \chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) \\
& + v(\underset{\sim}{q}')\, n_{\underset{\sim}{k}'\sigma'}\Big\{ D_2^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2}, \underset{\sim}{k}'-\frac{\underset{\sim}{q}'}{2}; q, q'\Big) - D_2^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2}, \underset{\sim}{k}'+\frac{\underset{\sim}{q}'}{2}; q, q'\Big)\Big\} \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) \\
& + \chi^{r0}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) .
\end{aligned} \qquad (4.4.30)$$

Equations (4.4.28) and (4.4.22b) together with equation (4.4.3) give,

$$\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega) = \Big\{ \phi_{ext}(\underset{\sim}{q}+\underset{\sim}{q}',\omega) + v(\underset{\sim}{q}+\underset{\sim}{q}')\,\bar{n}(\underset{\sim}{q}+\underset{\sim}{q}',\omega)\Big\} \cdot \frac{\bar{K}(\underset{\sim}{q},\underset{\sim}{q}',\omega)}{1 - \big\{ v(q)\,\chi^{r0}(\underset{\sim}{q},\omega) + v(q')\,\chi^{r0}(\underset{\sim}{q}',\omega)\big\}} . \qquad (4.4.31)$$

we can use this to obtain

$$\frac{1}{n_v}\sum_{q'} v(q')\,\bar{D}^{(2)}(q-q',q',\omega)\,\chi^{r0}(q,q',\omega)$$

$$= \frac{1}{n_v}\{\phi_{ext}(q,\omega)+v(q)\bar{n}(q,\omega)\}\sum_{q'}\frac{v(q')\chi^{r0}(q,q',\omega)\,\bar{K}(q-q',q',\omega)}{1-\{v(q-q')\chi^{r0}(q-q',\omega)+v(q')\chi^{r0}(q',\omega)\}}. \qquad (4.4.32)$$

Substituting in equation (3.1.9), we get an expression for $\chi^{r}(q,\omega)$ as,

$$\chi^{r}(q,\omega) = \frac{\chi^{r0}(q,\omega)+\chi^{2}(q,\omega)}{1-v(q)\{\chi^{r0}(q,\omega)+\chi^{2}(q,\omega)\}-\frac{1}{n_v}\sum_{q'}v(q')\{S(q-q')-1\}\chi^{r0}(q,q',\omega)}, \qquad (4.4.33)$$

$$\chi^{2}(q,\omega) = \frac{1}{n_v}\sum_{q'}\frac{v(q')\chi^{r0}(q,q',\omega)}{1-\{v(q-q')\chi^{r0}(q-q',\omega)+v(q')\chi^{r0}(q',\omega)\}}\cdot\bar{K}(q-q',q',\omega). \qquad (4.4.34)$$

This is the first and the simplest approximation that can be obtained in this approach. We can improve upon this by solving the integral equations for $M_{k\sigma}$ and $N_{k'\sigma'}$, which can be constructed from equation (4.4.23), making approximations like the ones in equations (4.4.27) in them.

The leading order contribution to $\chi^{2}(q,\omega)$ is obtained if we neglect the denominator in equation (4.4.34). (This would amount to retaining only the first term on the right hand side of equation (4.4.23)). Within this approximation, we can further simplify $\chi^{2}(q,\omega)$ using the expression for $\bar{K}(q,q',\omega)$. The last term (i.e., the $\chi^{r0}(q+q',\omega)$ term appearing

in $\bar{K}$ in equation (4.4.30)) gives zero contribution to $\chi^2(\underset{\sim}{q},\omega)$ which can be easily shown by making use of the fact that $\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ is an odd function of $\underset{\sim}{q}'$. We have already discussed in Section 4.3, the approximation in which the first two terms in $\bar{K}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ reduce to $\chi^{no}(q,\omega)$ (defined in equation (4.1.28)). In the remaining terms of $\bar{K}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$, we replace $\sum_{\underset{\sim}{k}'\sigma'} f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$ by the RPA expression

$$\sum_{\underset{\sim}{k}'\sigma'} f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = -n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - \frac{\hbar V}{\pi}\int_0^\infty d\omega\ \mathrm{Im}\left(\frac{\chi^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)}{\epsilon^r(\underset{\sim}{q},\omega)}\right), \quad (4.4.35)$$

which is derived in detail in the next Section. With the above substitution in the remaining four terms in the expression (4.4.30) for $\bar{K}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$, we obtain,

$$\chi^2(q,\omega) = \chi^1(q,\omega) + \frac{1}{nV}\sum_{\underset{\sim}{q}'} v(q')\,\chi^{ro}(\underset{\sim}{q},\underset{\sim}{q}',\omega)(-i\hbar)\sum_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}$$

$$\Bigg[v(\underset{\sim}{q}-\underset{\sim}{q}')\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,e^{-i\omega'\delta}\,\frac{\chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}-\underset{\sim}{q}',\omega')}{\epsilon^c(\underset{\sim}{q}-\underset{\sim}{q}',\omega')}\cdot\Big\{D_2^{-1}\Big(\underset{\sim}{k},\underset{\sim}{k}'+\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big)$$

$$- D_2^{-1}\Big(\underset{\sim}{k},\underset{\sim}{k}'-\frac{\underset{\sim}{q}-\underset{\sim}{q}'}{2};q-q',q'\Big)\Big\}\,\chi^{ro}_{\underset{\sim}{k}'\sigma'}(q,\omega)$$

$$+ v(\underset{\sim}{q}')\int_{-\infty}^{\infty}\frac{d\omega'}{2\pi}\,e^{-i\omega'\delta}\,\frac{\chi^{co}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}',\omega')}{\epsilon^c(-q',\omega')}\Big\{D_2^{-1}\Big(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big)$$

$$- D_2^{-1}\Big(\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2},\underset{\sim}{k}';\underset{\sim}{q}-\underset{\sim}{q}',\underset{\sim}{q}'\Big)\Big\}\,\chi^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\Bigg]. \quad (4.4.36)$$

The second term in $\chi^2(\underset{\sim}{q},\omega)$ does resemble $\chi^{A'}(\underset{\sim}{q},\omega)$, Here too we have a mode coupling term, though in the present case we have one unscreened response function coupling with a screened

$\chi^r(q,\omega)$, whereas in the earlier approximation (discussed in Section 4.1), the coupling is between screened functions. The reason for this is that in the former case we actually solved the RPA-integral equation in the presence of an external field whereas in the approach in this section, we have used response theory and reatined only leading order terms (i.e., we have not solved the integral equation here). In this sense the earlier approach is more general than the present one, and contains the full mode coupling feature.

Comparing equation (4.4.34) with equation (4.3.15), we find that the former equation reduces to the latter if we neglect the terms in the denomiator on the right hand side of (4.4.34). Thus we see that we have included self energy terms (as discussed in section 4.3), in our approach. It is this inclusion of higher order coorelations in our approach that gives rise to the mode coupling term. This is not surprising because the inclusion of the self energy effect does mean coupling between all the modes of the interacting electron system. We emphasize here that this aspect is completely missed out in the work of Aravind et al.[10] Further, judging from the calculation of long wavelength plasmon damping coefficient in Section 4.2 and its comparison with the perturbative calculation of Dubois and Kivelson[7], it appears to us that this aspect is very important as far as the damping of plasmons is concerned.

4.5 EVALUATION OF $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}$

A quantity that remains unknown in all these calculations is $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$. Other workers like Aravind et al.[10] have used ansätze which are so chosen that they satisfy the exact condition,

$$S(\underset{\sim}{q}) - 1 = \frac{1}{N}\sum_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'} f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) \,. \qquad (4.5.1)$$

We make an attempt here to obtain an expression for this equilibrium function, using the equation of motion approach. We start with the definition for $f^{(2)eq}$, equation (4.4.29),

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = \left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) \right\rangle_{eq} - \delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\, n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} \qquad (4.5.2)$$

As discussed in Appendix I, $\langle \hat{\tilde{\rho}}_{k\sigma}(q)\, \hat{\tilde{\rho}}_{k'\sigma'}(-q) \rangle_{eq}$ is related to the imaginary part of the retarded function (equation (A.1.16)) ; we have,

$$\left\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) \right\rangle_{eq} = -\frac{\hbar V}{\pi}\int_0^\infty d\omega\ \mathrm{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) \,. \qquad (4.5.3)$$

Then the equilibrium function is given by,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = -\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\, n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - \frac{\hbar V}{\pi}\int_0^\infty d\omega\ \mathrm{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) \qquad (4.5.4)$$

We obtain an expression for $\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ via the equation of motion method. From the definition of $\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t)$ given in equation (4.4.14),

$$i\hbar\frac{\partial}{\partial t}\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t) = \frac{1}{V}\delta(t)\left\langle \left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}),\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\right]_- \right\rangle_{eq}$$
$$+ \frac{\theta(t)}{V}\left\langle \left[\frac{\partial\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)}{\partial t},\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\right]_- \right\rangle_{eq} ,$$

$$= \frac{\delta(t)}{V}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\,\delta_{\sigma\sigma'}\,(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})$$

$$+ \frac{\Theta(t)}{V}\left\langle\left[\frac{\partial\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)}{\partial t}\,,\ \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},0)\right]_-\right\rangle_{eq}, \qquad (4.5.5)$$

where we have used expression (A.6.2) of Appendix VI to simplify the first term. The equation of motion for $\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$ using the Hamiltonian given by equation (4.4.8) is given by, (see equation (4.4.9)),

$$i\hbar\frac{\partial}{\partial t}\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})\,\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$$

$$+\frac{1}{V}\sum_{\underset{\sim}{q}_1} v(\underset{\sim}{q}_1)\,\hat{\rho}(\underset{\sim}{q}_1,t)\left[\hat{\rho}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t) - \hat{\rho}_{\underset{\sim}{k}+\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1,t)\right]. \qquad (4.5.6)$$

This leads to higher order correlations entering equation (4.5.5). We therefore make the mean field or RPA approximation in equation (4.5.6), itself by replacing the density operators by their equilibrium average values i.e.,

$$\hat{\rho}(\underset{\sim}{q},t) \longrightarrow \langle\hat{\rho}(\underset{\sim}{q},t)\rangle_{eq} = N\delta_{\underset{\sim}{q},0}\ ,$$

and $$\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) \longrightarrow \langle\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\rangle_{eq} = n_{\underset{\sim}{k}\sigma}\,\delta_{\underset{\sim}{q},0}\ .$$

Thus with RPA, equation of motion for $\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$ reduces to,

$$i\hbar\frac{\partial}{\partial t}\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})\,\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) + \frac{v(q)}{V}(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\,\hat{\tilde{\rho}}(\underset{\sim}{q},t). \qquad (4.5.7)$$

Taking Fourier transform with respect to time in equation (4.5.5) we get,

$$[\hbar\omega - \frac{\hbar^2}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q})]\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \frac{1}{V}\,\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\,(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})$$

$$+\frac{v(q)}{V}(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\sum_{\underset{\sim}{k}_1\sigma_1}\chi^{r}_{\underset{\sim}{k}_1\sigma_1\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\ ,$$

$$\Rightarrow \quad \chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\,\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)$$

$$+\frac{v(q)}{V}\,\frac{(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}-n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})}{\hbar\omega-(\hbar^2/m)(\underset{\sim}{k}.\underset{\sim}{q})}\sum_{\underset{\sim}{k}_1\sigma_1}\chi^{r}_{\underset{\sim}{k}_1\sigma_1,\,\underset{\sim}{k}'\sigma'}(q,\omega)\,. \qquad (4.5.8)$$

From equation (4.5.8) it is very easily seen that

$$\sum_{\underset{\sim}{k}\sigma}\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \frac{\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)}{1-v(q)\chi^{r0}(\underset{\sim}{q},\omega)}\,, \qquad (4.5.9)$$

Then using this is (4.5.8),

$$\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\left[\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}+\frac{v(q')\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(q,\omega)}{\epsilon^{r}(\underset{\sim}{q},\omega)}\right] \qquad (4.5.10)$$

We note here that $\chi^{r0}(\underset{\sim}{q},\omega)$ is the retarded density-density response function for the non-interacting system when $n_{\underset{\sim}{k}\sigma}$ is replaced by $n^{o}_{\underset{\sim}{k}\sigma}$, and $\epsilon^{r}(\underset{\sim}{q},\omega)$ is the corresponding RPA expression for the longitudinal dielectric function. Note that summation over $\underset{\sim}{k}\sigma$ and $\underset{\sim}{k}'\sigma'$ in equation (4.5.9) yields,

$$\chi^{r}(\underset{\sim}{q},\omega) = \frac{\chi^{r0}(\underset{\sim}{q},\omega)}{1-v(q)\chi^{r0}(\underset{\sim}{q},\omega)}\,,$$

the well-known RPA result for the retarded density-density response function of the interacting system. Equation (4.5.9) can also be written as,

$$\sum_{\underset{\sim}{k}\sigma}\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\,/\,\epsilon^{r}(\underset{\sim}{q},\omega)\,. \qquad (4.5.11a)$$

Similarly we have,

$$\sum_{\underset{\sim}{k}'\sigma'}\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\,/\,\epsilon^{r}(\underset{\sim}{q},\omega)\,. \qquad (4.5.11b)$$

Equation (4.5.10) suggests a method for obtaining $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$. If we replace the dielectric function in this equation by its general expression (2.1.10), we obtain,

$$\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\Big[\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'} + v(q)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) + v^{2}(\underset{\sim}{q})\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\,\chi^{r}(\underset{\sim}{q},\omega)\Big]. \qquad (4.5.12)$$

This equation though is quite complicated. Equations (4.5.11) suggest a much simpler approximation for $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$, i.e.,

$$\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\;\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)/\epsilon^{r}(\underset{\sim}{q},\omega), \qquad (4.5.13)$$

which is much simpler to handle. The virtue of the above approximation is that relations (4.5.11) are still valid, thus ensuring that this form for $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ gives the correct form for $\chi^{r}(\underset{\sim}{q},\omega)$ and the static structure factor, although it differs considerably from (4.5.12).

We use expression (4.5.10) for $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$. In this case the imaginary part of the function $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ is given by

$$\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\left(-\frac{\pi}{n\nu}\right)\left(n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\right)\delta\left(\omega - \frac{\hbar}{m}\underset{\sim}{k}\cdot\underset{\sim}{q}\right) + v(q)\,\mathrm{Im}\left(\frac{\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)}{\epsilon^{r}(\underset{\sim}{q},\omega)}\right), \qquad (4.5.14)$$

where we have used the expression for $\mathrm{Im}\,\chi^{r0}_{k\sigma}(q,\omega)$.

As shown in Appendix I,

$$\left[\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\right]^{*} = \chi^{r0}_{-\underset{\sim}{k}\sigma}(\underset{\sim}{q},-\omega) = \chi^{r0}_{k\sigma}(-\underset{\sim}{q},-\omega); \qquad (4.5.15a)$$

$$\left[\chi^{r0}(\underset{\sim}{q},\omega)\right]^{*} = \chi^{r0}(-\underset{\sim}{q},-\omega) = \chi^{r0}(\underset{\sim}{q},-\omega); \qquad (4.5.15b)$$

and

$$\left[\chi^{r}(\underset{\sim}{q},\omega)\right]^{*} = \chi^{r}(-\underset{\sim}{q},-\omega) = \chi^{r}(\underset{\sim}{q},-\omega). \qquad (4.5.15c)$$

Using these relations and equation (4.5.14) in the expression (4.5.3), we have,

$$\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}) \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) \rangle_{eq} = -\frac{\hbar V}{\pi} \int_0^\infty d\omega \; \mathrm{Im}\, \chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$$

$$= (n_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\,\Theta(\underset{\sim}{k}\cdot\underset{\sim}{q})\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\,\delta_{\sigma\sigma'}$$

$$- v(q)\,\frac{\hbar V}{2\pi} \int_0^\infty d\omega \left[\frac{\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)}{\epsilon^r(\underset{\sim}{q},\omega)} - \frac{\chi^{r0}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q},-\omega)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},-\omega)}{\epsilon^r(\underset{\sim}{q},-\omega)} \right]. \qquad (4.5.16)$$

Usually $n_{\underset{\sim}{k}\sigma}$ is not known in a simple analytic form and one replaces it by the free particle form $n^0_{\underset{\sim}{k}\sigma} = \Theta(k_F - k)$. With this replacement, the first term on the right hand side of the above equation can be simplified to,

$$(n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n^0_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma})\,\Theta(\underset{\sim}{k}\cdot\underset{\sim}{q}) = (n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma} - n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\, n^0_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}) \qquad (4.5.17)$$

Substituting (4.5.17) into (4.5.16) and then using this (4.5.16) in equation (4.5.4) we have,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) \cong \left[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) \right]^{HF}$$

$$- v(q)\,\frac{\hbar V}{2\pi} \int_0^\infty d\omega \left[\frac{\chi^{r0}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}',\omega)}{\epsilon^r(\underset{\sim}{q},\omega)} - \frac{\chi^{r0}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q},-\omega)\,\chi^{r0}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},-\omega)}{\epsilon^r(\underset{\sim}{q},-\omega)} \right]. \qquad (4.5.18)$$

Here,

$$\left[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) \right]^{HF} = -\delta_{\sigma\sigma'}\,\delta_{\underset{\sim}{k},\underset{\sim}{k}'}\, n^0_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\, n^0_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma},$$

is the form for the non-interacting free particle system. The second term in the equation gives an improvement over this non-interacting system result.

The ansätze for $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$ that Aravind et al.[10] chose are as given below,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = \left[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\right]^{HF} + \frac{1}{N}\,n^{0}_{\underset{\sim}{k}\sigma}\,n^{0}_{\underset{\sim}{k}'\sigma'}\{S(\underset{\sim}{q}) - S^{HF}(\underset{\sim}{q})\}\,, \quad (4.5.19a)$$

and

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) = \left[f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\right]^{HF}$$

$$+ \frac{1}{2N}\left\{n^{0}_{k-q/2\sigma}\,n^{0}_{k'+q/2\sigma'} + n^{0}_{k+q/2\sigma}\,n^{0}_{k'-q/2\sigma'}\right\}\{S(q) - S^{HF}(q)\}\,. \quad (4.5.19b)$$

On comparing with the form (4.5.18) that we have derived here, the ansätze chosen are found to be very different in form. They satisfy the exact requirement (4.5.1) exactly.

Another significant point that we would like to make about $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ is that, for the two particle equilibrium distribution function,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) = f^{(2)eq}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\,. \quad (4.5.20)$$

This follows directly from the definition (4.5.4), if we use a similar relation for $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ obtained in Appendix I (equation (A.1.12)). Most workers like Nikasson[8] and Aravind et al.[10], have assumed that $f^{(2)eq}$ is an even function of q, i.e., they assumed that,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) = f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\,.$$

As is obvious from equation (4.5.19) this assumption is incorrect and could lead to erroneous results. However, the ansätze chosen by Aravind et al.[10] (equations (4.5.19))

are such that the $f^{(2)eq}$ is an even function of q'. The expression for $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$ obtained by us (following the equation of motion approach and working within the RPA) is seen to satisfy the condition (4.5.20). We have however, not been able to use this approximation for $f^{(2)eq}$ for numerical calculations because of the enormous amount of computation required.

4.6 DISCUSSION

We have developed a theory for a complex frequency dependent local field correction, thus taking into account the dynamics of the exchange and correlation hole formed around each electron in a homogeneous electron system in the presence of a weak external perturbation. We used the equation of motion approach, truncating the series of coupled equations by approximating for the two particle distribution function appearing in the equation of motion for the one particle function. The decoupling of the two particle function had been carried out following the often used method of classical liquids which is given by

$$f^{(2)}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t) \cong f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{r},t)\, f^{(1)}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{r}',t) + \frac{1}{n^2}\sum_{\substack{\underset{\sim}{k}\sigma\\ \underset{\sim}{k}'\sigma'}} f^{(2)}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t). \qquad (4.6.1)$$

The solution could then be obtained in a self-consistent manner. Instead we have used different approximations for $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ $(= \sum_{\substack{\underset{\sim}{k}\sigma\\ \underset{\sim}{k}'\sigma'}} f^{(2)}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t)$, and solved the

equation for $f^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\omega)$ which led to an expression for $\bar{n}(q,\omega)$, the induced density, and hence the response function. It was seen that simple approximations for $C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ lead very easily to earlier results obtained by other workers who used very different approaches.

The first approximation that we studied, used an ad-hoc approximation suggested by Singwi et al. (SSTL)[6] for the vertex function appearing in the integral equation for the time-ordered density-density correlation function. The density-density correlation function $\bar{D}^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ was then obtained from the time-ordered function. The expression for the response function thus obtained contained a frequency dependent local field correction $G(\underset{\sim}{q},\omega)$. In the classical limit ($\hbar \to 0$), if we neglect the dynamic screening, we obtain the same local field expression as that of SSTL[6]. We retained the frequency dependence in the local field correction and carried out numerical calculations in the classical limit. The local field was seen to be a sum of two quantities, one, the static local field obtained earlier by Singwi et al. (STLS)[31] and the other a complex, frequency dependent quantity.

The frequency dependence of the imaginary part of the local field was found to be controlled by a factor of the type $Q^{r'}{}'Q^{r''}$ i.e. by coupling between the excitation modes of the system. This feature had earlier been observed in a mode coupling theory developed earlier by Sharma et al.[10] using

Mori formalism. Following the equation of motion approach, to our knowledge this has been the first time that coupling between modes has been incorporated into the theory. We calculated the damping coefficient for long wavelength plasmons using the polarisability for the interacting system (approximated by Q_{RPA}) as well as that for the non-interacting system (taking free particle Q^{ro}). Due to the screening included in the former case, the values for damping coefficient obtained there were much higher than those obtained in the latter case, for all r_s taken in the metallic density range. The results in the latter case were compared with the perturbative calculations in the weak coupling ($r_s \rightarrow 0$) limit and the agreement was seen to be quite fair.

We also calculated the real and imaginary parts of the local field correction for finite q and ω. The predicted behaviour in these cases as suggested by Niklasson[8] was seen to be fulfilled. The energy loss spectra i.e. $S(q,\omega)$ was calculated for one momentum transfer $q = 1.6$. Although the experimentally observed double peak structure was not present here, the peak in the present case did shift towards the experimental result. A high frequency tail in $S(q,\omega)$ was also observed. A drawback of this theory was that it gave the same value for the local field correction in the static as well as high frequency limits. The expression for $\bar{D}^{(2)}(\underset{\sim}{q},\underset{\sim}{q}',\omega)$ in this case was not symmetric, with respect to exchange of variables $\underset{\sim}{q}$ and $\underset{\sim}{q}'$ as required by the definition. The reason

for these drawbacks could be the ad-hoc nature of the approximation.

We improved upon this approximation by using the linear response theory to obtain the vertex function. In this case again the resultant local field was complex and frequency dependent. The damping coefficient for long wavelength plasmons had values higher than those obtained in the earlier approximation. The agreement with the weak coupling ($r_s \rightarrow 0$) limit perturbative calculations was much better. In this case also it was noticed that including the screening effect, reduced the damping coefficient considerably. One part of the local field could be identified with the local field obtained when $\bar{C}^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t)$ was extracted from the equation of motion of the two particle distribution function. We also developed a response function corresponding to $D^{(2)}$ in the presence of an external field and from its equation of motion also obtained $G(q,\omega)$. A similar $G(q,\omega)$ could be obtained by extracting $\bar{C}^{(2)}$ using another approximation in the two particle equation of motion. These two approaches and the expressions for local field obtained therefrom, showed that our theory included higher order correlation. These higher order correlations are responsible for the appearance of the mode coupling term which is absent in all other equation of motion approaches. Although the mode coupling feature follows more naturally from Mori formulation[53], one cannot extract the static properties there,

unlike the present case. Thus, the simple, systematic approach adopted here, the inclusion of higher order correlations and the damping of long wavelength plasmons are the improved aspects of this approach.

Finally, the expression for $f^{(2)eq}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})$ obtained here using the equation of notion approach is also an important contribution. No calculation could be carried out using this expression for $f^{(2)eq}$ because of the large amount of computation involved.

CHAPTER 5

DYNAMIC IMAGE POTENTIAL

We study here the interactions of a semi-infinite jellium (representative of a metal with a planar surface) with a moving charged particle or a neutral atom. Recent scattering experiments studying surface phenomena necessitate such a study. Analysis of experiments involving low electron energy diffraction (LEED), fast electron spectroscopy etc.[4], require a theoretical knowledge of dynamical image potential which is the interaction between a moving charged particle and a metal surface. Several attempts have been made to include the effect of velocity of the charged particle but it has been mainly restricted to the particles moving at a constant speed. We study here the effect of acceleration of the particle on the dynamic image potential.

The plan of this chapter is the following. In Section (5.1) we discuss broadly the two different approaches used in calculating the dynamic image potential. In Section (5.2) we develop the theoretical formulation for dynamic image potential V(z,v) in both these approaches taking acceleration of the particle also into account. Section (5.3) gives the calculations and results obtained for V(z,v). Finally Section (5.4) gives the conclusions based on the present study.

5.1 REVIEW

The electrostatic interaction of a fixed charge with a vacuum-metal interface can be represented by the method of images, well known in electrostatics. When the charge is moving, the interaction gives rise to the dynamic image potential whose origin is as follows. When a charged particle approaches a metal surface, elementary excitations in the form of particle-hole oscillations and charge density oscillations (plasma oscillations) are set up within the metal. The interaction of the charged particle with the electromagnetic fields associated with these excitations gives rise to the dynamic image potential. The importance of these excitations in the formation of image charges and thereby the potential is studied by a number of workers[62-65]. Since the response of the metal to the incoming particle is causal, the velocity of the incoming particle enters the theory.

There are broadly two theoretical approaches for evaluation of dynamic image potential - one, where the incoming charge is treated classically and the other where the particle is treated semi-classically and the excitations in the metal as quantised systems[66]. By the semi-classical treatment of the particle we mean the use of a high energy approximation where the unperturbed energy ϵ_o of the particle is assumed to be much larger than its average energy of interaction with the collective modes ; also its associated de Broglie wavelength

is regarded to be much smaller than the wavelengths of the excitations involved. Under these conditions, the particle appears to provide a quasi-infinite source of energy and momentum to the excitations in the metal. The particle can now be treated as a source of perturbation which is well localised in space with the time dependence given by the classical trajectory and the problem can then be formulated in terms of a model Hamiltonian. The two conditions mentioned above can be achieved either for a particle moving rapidly (i.e. high kinetic energy) as in fast electron spectroscopy or for low kinetic energy but high potential energy of the particle as in image charge phenomena. A number of workers have studied the dynamic image potential for the case of an electron approaching the metal surface using this model Hamiltonian approach[11-13,67,68]. On the other hand, treating the particle classically and using linear response theory one can obtain an expression for the dynamic image potential. This latter method, called the dielectric response approach, can incorporate in the formulation, the details (e.g., dispersion) of the excitations in themetal in a straightforward manner and thus has an advantage over the one described earlier.

In all the theories proposed using dielectric response approach[69-73] and in most of the model Hamiltonian approaches[67,68], it is assumed that the particle is moving at aconstant speed along a classical trajectory. In reality though, due to the

image potential, the particle is accelerated and its velocity gets modified. One should therefore take this modification into account. Earlier Ray and Mohan[13] employed a self-consistent scheme, using the energy conservation principle and in a rather ad-hoc manner replaced the constant speed of the particle by its local (instant) speed. They obtained substantial modifications in the image potential values even though they could not justify their ad-hoc approximation. In our calculations for the dynamic image potential we include the acceleration of the particle self consistently following the model Hamiltonian approach[11,62], and show how the local speed approximation enters the theory in a natural way. We also use the microscopic dielectric response approach and the semi-classical infinite barrier model[74] to obtain an expression for the image potential[75] where again we are able to show how the local speed enters the self-consistent scheme for calculation of image potential.

5.2 THEORETICAL FORMULATION

We consider a semi-infinite jellium model for the metal which extends in the $z > 0$ region with its surface perpendicular to the z-axis and located at $z = 0$. Here, the jellium approximation for the metal means that in the region $z > 0$, the metal is assumed to have a constant electron density which is coincident with the positive background of the jellium.

The charged particle is located in the vacuum ($z < 0$) region and is assumed to move towards the metal along the z-axis so that at any instant t, the particle coordinate is described by $\underset{\sim}{r}(t) = (0,0,z(t))$. Within this model we then obtain an expression for the dynamic image potential in both the approaches.

5.2.1 Model Hamiltonian approach

The two basic assumptions made in this approach are the following. (i) The charged particle interacts only with the surface plasmons (i.e. the charged particle does not create the bulk plasmons), and (ii) these surface plasmons are dispersionless (i.e. the plasmon frequencies are independent of the wavevector). The Hamiltonian for the interacting system of surface plasmons and the charged particle is given by

$$H = H_{oq} + H_{os} + H_I \,, \qquad (5.2.1)$$

where H_{oq} and H_{os} are the Hamiltonians of the unperturbed charged particle and the surface plasmons respectively and H_I denotes the interaction between them. H_I is given by,

$$H_I = \sum_{\underset{\sim}{k}} \Gamma_k \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}} \, e^{-k|z|} \, (a_{\underset{\sim}{k}} + a^{+}_{\underset{\sim}{k}}) \,. \qquad (5.2.2)$$

Here a^{+}_{k} and a_k are the creation and annihilation operators for the surface modes, $\underset{\sim}{k}$ is the two-dimensional Fourier wavevector (in the x-y plane) and Γ_k is the coupling constant given by[76-78],

$$\Gamma_k^2 = \frac{\pi q^2 \hbar \omega_s}{k} \,, \qquad (5.2.3)$$

125

q being the charge of the incoming particle and ω_s, the surface plasmon frequency given by $\omega_p/\sqrt{2}$, where ω_p is the classical plasma frequency for the metal.

The static image potential, i.e., the image potential due to a static charge placed at a distance z from the metal surface can be obtained very easily. In this case since the kinetic energy of the particle is zero, the Hamiltonian (5.2.1) can be written as, ($z < 0$),

$$H_0 = \sum_{\underset{\sim}{k}} \left[\hbar\omega_s \, a^{+}_{\underset{\sim}{k}} a_{\underset{\sim}{k}} + \Gamma_k \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}} \, e^{kz} \, (a_{\underset{\sim}{k}} + a^{+}_{\underset{\sim}{k}}) \right], \quad (5.2.4)$$

This may be solved by making a transformation that completes the square, i.e.,

$$H_0 = \sum_{\underset{\sim}{k}} \left[\hbar\omega_s \, \tilde{a}^{+}_{\underset{\sim}{k}} \tilde{a}_{\underset{\sim}{k}} - \frac{\Gamma_k^2}{\hbar\omega_s} \, e^{2kz} \right],$$

where,

$$\tilde{a}_{\underset{\sim}{k}} = a_{\underset{\sim}{k}} + \frac{\Gamma_k}{\hbar\omega_s} \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}} \, e^{kz} .$$

The last term in H_0 is the self energy which gives the static image potential,

$$V(z) = - \sum_{\underset{\sim}{k}} \frac{\Gamma_k^2}{\hbar\omega_s} \, e^{2kz} ,$$

$$= - \frac{q^2}{4z} , \qquad \text{for } z < 0. \quad (5.2.5)$$

This is the classical static image charge result.

The case which is of greater relevance but more difficult to handle theoretically is that of a moving charge. An exact solution in this case is not possible and approximations have to be resorted to. In the interaction

representation, the wave function for such a system (i.e., the moving charge interacting with the surface plasmons) has the time development given by,

$$i\hbar \frac{\partial}{\partial t} \psi(t) = H_I(t)\,\psi(t) ,$$
$$= \sum_{\underset{\sim}{k}} \Gamma_k \, e^{kz(t)} \left(a_k . e^{i\omega_s t} + a_k^\dagger e^{-i\omega_s t} \right) . \qquad (5.2.6)$$

If we assume that the particle initially started at $t = -\infty$ with $z = -\infty$, the solution for (5.2.6) is given by,

$$\psi(t) = \exp\left[-i \sum_k \left\{ I_k(t)\, a_k + I_k^*(t)\, a_k^\dagger \right\} \right] \psi(-\infty) , \qquad (5.2.7)$$

where,

$$I_k(t) = \Gamma_k \int_{-\infty}^{t} dt' \; e^{kz(t')} \; e^{i\omega_s t'} . \qquad (5.2.8)$$

Using the operator identity,

$$e^{A+B} = e^A . e^B . e^{-\frac{1}{2}[A,B]_-} , \qquad (5.2.9)$$

(applicable when $[A,B]_-$ is a c-number), and assuming zero temperatures so that $\psi(-\infty)$ is the ground state $|0\rangle$, we get,

$$\psi(t) = \prod_k e^{-\frac{1}{2}|I_k(t)|^2} \; e^{-i I_k^*(t)\, a_k^\dagger} \, |0\rangle . \qquad (5.2.10)$$

The expectation value of the Hamiltonian H_0 given by (5.2.4) can be obtained using this wavefunction. Identifying the resulting expectation value with the induced self-energy of the charged particle or the dynamic image potential $V(z(t))$, we have,

$$V(z(t)) = \langle \psi(t) | \sum_{\underset{\sim}{k}} \left\{ \hbar\omega_s \, a_k^\dagger a_k + \Gamma_k \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}} \, e^{kz(t)} (a_k + a_k^\dagger) \right\} | \psi(t) \rangle , \qquad (5.2.11)$$
$$= \sum_k \hbar\omega_s \, |I_k(t)|^2 - 2 \sum_k \hbar\omega_s \, |I_k(t)|^2$$
$$= - \sum_k \hbar\omega_s \, |I_k(t)|^2$$
$$= - \hbar\omega_s \int \frac{d^2k}{(2\pi)^2} \, \Gamma_k^2 \left| \int_{-\infty}^{t} dt' \; e^{kz(t') + i\omega_s t'} \right|^2 . \qquad (5.2.12)$$

This general expression can now be used to calculate image

potential for different approximations for time dependence in z(t). The simplest approximation for dynamic image potential would of course be obtained if we assumed that the charged particle was moving at a constant speed v. In this case then,

$$z(t) = vt \quad , \tag{5.2.13}$$

which is consistent with the assumption that at $t \to -\infty$, the particle was at $z \to -\infty$. Now the integral in $I_k(t)$ is very simple to evaluate, and we obtain

$$I_k(t) = \Gamma_k \quad \frac{e^{(kv+i\omega_s)t}}{kv+i\omega_s} \quad . \tag{5.2.14}$$

Using this in (5.2.12) we have,

$$V(z,v) = -\hbar^2 \omega_s^2 \pi q^2 \int \frac{d^2k}{(2\pi)^2} \cdot \frac{1}{k} \frac{e^{2kvt}}{k^2v^2+\omega_s^2} \quad . \tag{5.2.15}$$

This integral cannot be performed analytically but can be written in terms of a standard listed integral f(x)[79].

Thus,

$$V(z,v) = -\frac{q^2\hbar^2\omega_s}{2v} \cdot f\left(\frac{2|z|\omega_s}{v}\right), \tag{5.2.16}$$

where,

$$f(x) = \int_0^\infty d\alpha \quad \frac{e^{-\alpha x}}{1+\alpha^2} \quad . \tag{5.2.17}$$

This result has been obtained by different authors employing different approaches[11,65,67,69-73].

An improvement over the constant speed approximation was made by Ray and Mahan[13]. They just replaced the constant speed v appearing in (5.2.16) by the local speed v(z) of the particle. This local speed v(z) was in turn obtained self-consistently from the energy conservation principle,

$$\frac{1}{2}mv_0^2 = \frac{1}{2}mv^2 + V(z,v) \quad , \tag{5.2.18}$$

where v_o is the initial speed of the particle. This ad-hoc simple approximation yields considerable modifications in $V(z,v)$ over the constant speed results.

In the present study, we incorporate the acceleration of the particle into this model Hamiltonian approach. As the particle approaches the metal surface, the induced attractive image potential attracts the particle thus accelerating it. Since in the first approximation, the image potential is inversely proportional to the speed of the particle, this increase in velocity leads to a reduction in the image potential values. This in turn reduces the acceleration and so on till a balance is achieved. Hence, to take into account the acceleration, we have performed iterative calculations as in the self-consistent method[13]. The exact procedure is described below.

We assume in anticipation that the variation of acceleration with respect to time is much less than that of the speed, so that a truncation of the Taylor series expansion of $z(t')$ about t as,

$$z(t') = z(t-t_1) \cong z(t) - t_1 \dot{z}(t) + t_1^2 . \ddot{z}(t)/2 ,$$
$$\cong z(t) - v(t) . t_1 + a(t) . t_1^2/2 , \qquad (5.2.19)$$

is possible. In equation (5.2.19), a is the acceleration and v the speed of the particle. Substituting this expansion for $z(t)$ in equation (5.2.8) for $I_k(t)$, we have,

$$I_k(t) = \Gamma_k \int_{-\infty}^{t} dt' \; e^{kz(t') + i\omega_s t'} ,$$
$$= \Gamma_k \int_{0}^{\infty} dt_1 \; e^{i\omega_s [t-t_1]} . e^{kz(t-t_1)} ,$$

$$= \Gamma_k \cdot e^{i\omega_s t} \; e^{kz(t)} \int_0^\infty dt_1 \, e^{-[kv(t) + i\omega_s]t_1} \cdot e^{\frac{k}{2} a(t) \, t_1^2} .$$

From the expression (5.2.8) for $I_k(t)$, it is evident that the major contribution to $I_k(t)$ comes from the region close to t, i.e., in the integral given above, the major contribution is from small values of t_1. To comply with this and to ensure convergence of the integral we replace $\exp(\frac{k\,a(t)}{2}\, t_1^2)$ by $1 + \frac{k\,a(t)}{2}\, t_1^2$. We note here that the latter approximation made for ensuring convergence is typical in the evaluation of the canonical partition function for anharmonic oscillators. The expression for $I_k(t)$, using this expansion, then becomes

$$I_k(t) = \Gamma_k \cdot e^{i\omega_s t + kz(t)} \int_0^\infty dt \, e^{-[kv(t) + i\omega_s]t_1} \cdot \left[1 + \frac{k\,a(t)}{2}\, t_1^2\right]. \quad (5.2.20)$$

Now the t_1 integral is easy to evaluate and we obtain

$$I_k(t) = \Gamma_k \, e^{i\omega_s t + kz} \left[\frac{1}{kv + i\omega_s} + \frac{ak}{(kv + i\omega_s)^3} \right] . \quad (5.2.21)$$

Here we have dropped the t-dependence from z, v and a for brevity.

The image potential in this case is then given by,

$$V(z, v) = -q^2\hbar^2 \omega_s^2 \int_0^\infty dk \; e^{2kz} \left[\frac{1}{k^2v^2 + \omega_s^2} + \frac{2ak(k^2v^2 - \omega_s^2)}{(k^2v^2 + \omega_s^2)^3} \right]. \quad (5.2.22)$$

Defining $\alpha = kv/\omega_s$, $\lambda = a/v\omega_s$ and $x = -2\omega_s z/v$, we rewrite V(z,v) as,

$$V(z, v) = -\frac{q^2\hbar^2\omega_s}{2v} \int_0^\infty d\alpha \; e^{-\alpha x} \left[\frac{1}{\alpha^2 + 1} + \frac{2\lambda\alpha(\alpha^2 - 1)}{(\alpha^2 + 1)^3} \right],$$

$$= -\frac{q^2\hbar^2\omega_s}{2v} \left[f(x) - \frac{\lambda x}{2} \left\{ f(x) + x \, \frac{df(x)}{dx} \right\} \right] . \quad (5.2.23)$$

In equation (5.2.23), f(x) is the same standard integral defined in equation (5.2.17). As can be seen very easily,

putting $a = 0$ or $\lambda = 0$, we get back the constant speed expression (5.2.16) with constant v replaced by the local speed v(t). Thus we are also able to give a theoretical justification for the ad-hoc approximation (i.e. replacement of constant speed by local speed) made by Ray and Mahan[13].

An expression for the acceleration can be obtained by making use of the classical equation of motion

$$ma = -\frac{dV}{dz} \qquad (5.2.24)$$

In (5.2.24), neglecting the variation in 'a', the acceleration, compared with that of v, as a function of z, we obtain,

$$\lambda = -\frac{\frac{df}{dx}}{\frac{mv^3}{q^2\omega_s} - \left(x\frac{df}{dx} + \frac{x^2}{2}\frac{d^2f}{dx^2}\right)} \; . \qquad (5.2.25)$$

The local velocity v is again obtained from the energy conservation principle (5.2.18). Starting with acceleration equal to zero, we can then obtain the dynamic image potential by solving iteratively equations (5.2.23), (5.2.25) and (5.2.18). Details of the numerical results are given in Section (5.3).

We note here that V(z,v) has the maximum potential depth (see equation (5.2.23)) at the metal surface i.e., at $z = 0$. In the present case, the term $\frac{\lambda x}{2}\left\{f(x) + x\frac{df}{dx}\right\}$, which is a correction to the constant speed image potential values, is always zero at $x = 0$. This is obvious from the expressions (5.2.23) and (5.2.25) for V(z,v) and λ and the

following limiting conditions :

$$\lim_{x \to 0} f(x) = \frac{\pi}{2} \quad ; \qquad (5.2.26a)$$

and

$$\lim_{x \to 0} x \cdot \frac{df}{dx} = 0 \quad . \qquad (5.2.26b)$$

Hence in this case the value of V at the surface is the same as that obtained by Ray and Mahan[13]. The maximum potential depth that can be obtained is given by,

$$V_{max} = - \left(\frac{3\pi^2}{8}\right)^{1/2} r_s^{-1} \text{ Ryd.} \quad .$$

A quantity of interest that can be evaluated from the image potential values is Q, the average number of excitations excited at the metal surface. This Q is given by[11],

$$Q = - \frac{2V(z,v)}{\hbar\omega_s} \quad .$$

Maximum value of Q is,

$$Q_{max} = - \frac{2V_{max}}{\hbar\omega_s} = 1.263\, r_s^{1/2} \quad .$$

We take this opportunity to point out a small numerical error in the calculations carried out by Mahan in ref. 14 where the value of Q_{max} is reported as $2.5\, r_s^{-1/2}$. Q_{max} is an important quantity because it is measurable. The probability that the electron excites n excitations (here surface plasmons) simultaneously, is given by a Poisson protability distribution[66],

$$P_n = \frac{Q^n}{n!} e^{-Q} \quad , \qquad (5.2.27)$$

where Q is the same as defined above. From above then, the probability that the electron does not excite any excitations is $\exp(-Q_{max})$ and this is measurable[11].

5.2.2 Microscopic dielectric response approach

For a particle that can be treated classically, the dynamic image potential at its location $\underset{\sim}{r}(t)$ at any instant of time t is given by,

$$V(\underset{\sim}{r}(t)) = \frac{1}{2} q(t)\, V_i(\underset{\sim}{r}_0(t)) \,. \qquad (5.2.28)$$

Here, V_i is the Coulomb potential due to the charge density n_i induced in the metal by the external charge q(t) (where for generality, we have kept a time dependence in q), i.e.,

$$V_i(\underset{\sim}{r}, t) = \int \frac{d^3r'}{|\underset{\sim}{r} - \underset{\sim}{r}'|}\, n_i(\underset{\sim}{r}', t) \,. \qquad (5.2.29)$$

The induced density n_i, within the linear response theory is given by,

$$\begin{aligned} n_i(\underset{\sim}{r}', t) &= \int d\underset{\sim}{r}'' \int_{-\infty}^{\infty} dt'\, \chi^r(\underset{\sim}{r}', \underset{\sim}{r}'', t-t')\, V_{ext}(\underset{\sim}{r}'', t'), \\ &= \int d\underset{\sim}{r}'' \int_{-\infty}^{\infty} dt'\, \chi^r(\underset{\sim}{r}', \underset{\sim}{r}'', t-t')\, \frac{q(t')}{|\underset{\sim}{r}'' - \underset{\sim}{r}_0(t')|} \,, \qquad (5.2.30) \end{aligned}$$

where χ^r is the retarded density-density response function for the metal with surface. Thus the determination of image potential now reduces to the determination of χ^r. The $\chi^r(\underset{\sim}{r}', \underset{\sim}{r}'', t-t')$ can be expressed in terms of its time and two dimensional spaces Fourier transform (in x - y plane, where the metallic system has translational invariance), i.e.,

$$\chi^r(\underset{\sim}{r}', \underset{\sim}{r}'', t) = \int \frac{d^2k}{(2\pi)^2}\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}' - \underset{\sim}{\rho}'')} \frac{d\omega}{2\pi}\, e^{-i\omega t}\, \chi^r(\underset{\sim}{k}, z', z'', \omega), \qquad (5.2.31)$$

where $\underset{\sim}{\rho}'$ and $\underset{\sim}{\rho}''$ refer to the polar coordinate in x-y plane. Using this, we have,

$$n_i(\underset{\sim}{r}', t) = \int \frac{d^2k}{(2\pi)^2} \cdot \frac{d\omega}{2\pi}\, dz''\, dt'\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}' - \underset{\sim}{\rho}'') - i\omega(t-t')} \cdot \frac{d^2\underset{\sim}{\rho}''\, q(t')\, \chi^r(\underset{\sim}{k}, z', z'', \omega)}{\sqrt{(\underset{\sim}{\rho}'' - \underset{\sim}{\rho}(t'))^2 + (z'' - z(t'))^2}},$$

$$= \int \frac{d^2k}{(2\pi)^2}\, \frac{d\omega}{2\pi}\, dz''\, dt'\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}' - \underset{\sim}{\rho}_0(t')) - i\omega(t-t')} \cdot \chi^r(\underset{\sim}{k}, z', z'', \omega) \cdot \frac{2\pi q(t')}{k}\, e^{-k|z'' - z(t')|}. \quad (5.2.32)$$

Substituting this expression back in equation (5.2.29),

$$V_i(\underset{\sim}{r}, t) = \int \frac{d^2k}{(2\pi)^2}\, \frac{d\omega}{2\pi}\, dz''\, dt'\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}' - \underset{\sim}{\rho}_0(t')) - i\omega(t-t')} \cdot \chi^r(\underset{\sim}{k}, z', z'', \omega) \cdot q(t') \cdot \frac{2\pi}{k}\, \frac{e^{-k|z'' - z_0(t')|}}{\sqrt{(\underset{\sim}{\rho} - \underset{\sim}{\rho}')^2 + (z - z')^2}}\, d^2\rho'\, dz',$$

$$= \int \frac{d^2k}{(2\pi)^2} \cdot \frac{d\omega}{2\pi} \cdot \frac{2\pi}{k}\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho} - \underset{\sim}{\rho}_0(t')) - i\omega(t-t')}\, dt' \cdot q(t')\, dz'\, dz'' \cdot \frac{2\pi}{k} \cdot e^{-k|z-z'|}\, \chi^r(\underset{\sim}{k}, z', z'', \omega)\, e^{-k|z'' - z_0(t')|}. \quad (5.2.33)$$

To obtain the above forms of the expression we have repeatedly used the translational invariance of the system in the x-y plane alongwith the definitions of temporal and 2-dimensional space Fourier transforms. Substituting above form for $V_i(\underset{\sim}{r}(t))$ in equation (5.2.28),

$$V(\underset{\sim}{r}, t) = \frac{q(t)}{2} \int \frac{d^2k}{(2\pi)^2}\, \frac{d\omega}{2\pi}\, dt' \cdot \frac{2\pi}{k}\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho} - \underset{\sim}{\rho}_0(t')) - i\omega(t-t')}\, q(t')\, \mathcal{F}(\underset{\sim}{k}, z, z(t'), \omega),$$

where

$$\mathcal{F}(\underset{\sim}{k}, z, z(t'), \omega) = \frac{2\pi}{k} \int dz'\, dz''\, e^{-k|z'-z|}\, \chi^r(\underset{\sim}{k}, z', z'', \omega)\, e^{-k|z'' - z_0(t')|}.$$

The problem now is of determining $\mathcal{F}$ from χ^r. Some more simplifications are however possible in the present situation, χ^r vanishes for z' or z'' outside the metal and also its retarded nature requires t' < t. Thus for a charged particle outside the metal as in the present case, z'-z > 0,

$z'' - z(t') > 0$ for z and $z(t') < 0$, so that,

$$V(\underset{\sim}{r}(t)) = \frac{q(t)}{2} \int \frac{d^2k}{(2\pi)^2} \cdot \frac{d\omega}{2\pi} \cdot \frac{2\pi}{k} \, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho} - \underset{\sim}{\rho}_0(t')) - i\omega(t-t')} \cdot q(t') \cdot e^{kz + kz_0(t')} \cdot F(\underset{\sim}{k}, \omega) \, dt' \qquad (5.2.34)$$

where,

$$F(\underset{\sim}{k}, \omega) = \frac{2\pi}{k} \int dz' \int dz'' \, e^{-k|z' + z''|} \, \chi^r(\underset{\sim}{k}, z', z'', \omega) . \qquad (5.2.35)$$

where the order of integration should be maintained.

Determination of the form factor $F(k,\omega)$ requires χ^r which is a very difficult task even with the simple model of a semi-infinite jellium and within the random phase approximation. This is because in RPA, the retarded density-density response function χ^r for the interacting system is determined from the integral equation

$$\chi^r(\underset{\sim}{k}, z, z', \omega) = \chi^{ro}(\underset{\sim}{k}, z, z', \omega) + \iint_{-\infty}^{\infty} dz_1 \, dz_2 \, \chi^{ro}(\underset{\sim}{k}, z, z_1, \omega) \, e^{-k|z_1 - z_2|} \, \frac{2\pi}{k} \, \chi^r(\underset{\sim}{k}, z_2, z', \omega).$$

where χ^{ro} corresponds to the retarded density-density response function for the non-interacting electron system. χ^{ro} can be constructed from one electron wave-functions for the semi-infinite jellium. However, for a realistic description of the jellium, the wave-functions can be obtained only in numerical form so that calculation of χ^r itself requires enormous computational effort. On the other hand, it is possible to simplify the problem a great deal if χ^{ro} is approximated at the expense of the quantitative accuracy. One such approximation is the semi-classical infinite barrier model[74,80] (SCIB).

The SCIB model which is an alternate description of the so called specular reflection model corresponds to the situation where the ground state electron density profile coincides with the positive background of the jellium. Following the construction suggested in the reference[74] we have for the SCIB model,

$$\chi^{ro}(\underset{\sim}{k}, z, z', \omega) = \int_{-\infty}^{\infty} \frac{dp}{2\pi} \chi_B^{ro}(q, \omega)\left[e^{ip(z-z')} + e^{ip(z+z')} \right],$$

for $z, z' > 0$. Here $q^2 = k^2 + p^2$ and $\chi_B^{ro}(q,\omega)$ refers to the response function of the non-interacting infinite electron system (jellium). Using this in the integral equation for χ^r, it is then possible to find an expression for the form factor $F(k,\omega)$ in a closed form given by, (detailed algebraic steps can be found in refs. 75 and 81),

$$F(\underset{\sim}{k}, \omega) = \frac{1 - \epsilon_s(\underset{\sim}{k}, \omega)}{1 + \epsilon_s(\underset{\sim}{k}, \omega)}, \qquad (5.2.36)$$

where

$$\epsilon_s^{-1}(\underset{\sim}{k}, \omega) = \frac{k}{\pi} \int_{-\infty}^{\infty} \frac{dp}{k^2 + p^2} \cdot \frac{1}{\epsilon_B(q,\omega)}, \qquad (5.2.37)$$

with $q^2 = k^2 + p^2$ and $\epsilon_B(q,\omega) = 1 - 4\pi e^2 \chi_B^{ro}(q,\omega)/q^2$, the RPA dielectric function for the infinite electron system having the bulk electron density. This form was obtained earlier by Heinrichs[70] who used additional boundary conditions which have been avoided in the present case. $\epsilon_s(k,\omega)$ is the surface dielectric function and contains information of all the excitations in the metal surface. For example, $1 + \epsilon_s(k,\omega) = 0$

corresponds to the dispersion relation for surface plasmons[82] which give the most dominant contribution to $F(k,\omega)$. Substituting equation (5.2.36) for $F(k,\omega)$ in equation (5.2.34), we get,

$$V(z(t)) = \frac{q(t)}{2} \int \frac{d^2k}{(2\pi)^2} \cdot \frac{d\omega}{2\pi} \frac{2\pi}{k} e^{i\underset{\sim}{k} \cdot (\underset{\sim}{\xi} - \underset{\sim}{\xi}_0(t')) - i\omega(t-t')} \cdot q(t') e^{kz + k\dot{z}_0(t')} \cdot \frac{1 - \epsilon_s(\underset{\sim}{k}, \omega)}{1 + \epsilon_s(\underset{\sim}{k}, \omega)} \quad (5.2.38)$$

We note that this formula is particularly useful when we want to go beyond the local approximation for $\epsilon_s(k,\omega)$, e.g., when one wants to take the dispersion of surface plasmons into account[75]. In the present study, as we are interested in studying the effects of the motion of the particle on the image potential values, we use the simplest approximation - the classical local approximation for $\epsilon_s(k,\omega)$, i.e.,

$$\epsilon_s(\omega) = 1 - \omega_p^2 / \omega^2 \quad (5.2.39)$$

This gives,

$$F_{cl}(k,\omega) = \omega_s^2 / (\omega^2 - \omega_s^2) \cdot \quad (5.2.40)$$

For the case of the dynamical image potential we have a charge of fixed strength approaching the surface ; hence $q(t) = q$. The geometry that we have chosen to study this phenomenon requires the charged particle to approach the surface along the z-axis, so that in this case,

$$V(z(t)) = \frac{q^2}{4\pi} \int_0^\infty dk \, dt_1 \, e^{kz + kz(t+t_1)} \cdot d\omega \cdot e^{-i\omega t_1} \cdot \frac{\omega_s^2}{\omega^2 - \omega_s^2} \cdot$$

Making a similar approximation for $\exp[kz(t+t_1)]$ as in the previous section we now obtain,

$$V(z,v) = \frac{q^2\omega_s}{2}\int_0^\infty dk\ e^{2kz(t)}\ \mathrm{Im}\int_{-\infty}^{0} dt_1\ e^{(i\omega_s + kv)t_1}\left(1+\frac{ka}{2}t_1^2\right),$$

$$= -\frac{q^2}{2}\int_0^\infty dk\cdot e^{2kz(t)}\left[\frac{1}{1+\frac{k^2v^2}{\omega_s^2}} + \frac{ka}{\omega_s^2}\cdot\frac{\left(3\frac{k^2v^2}{\omega_s^2}-1\right)}{\left(\frac{k^2v^2}{\omega_s^2}+1\right)^3}\right],$$

$$= -\frac{q^2}{2}\frac{\omega_s}{v}\int_0^\infty d\alpha\ e^{-\alpha x}\left[\frac{1}{\alpha^2+1} + \lambda\cdot\frac{\alpha(3\alpha^2-1)}{(\alpha^2+1)^3}\right], \quad (5.2.41)$$

where α, x, λ have been defined earlier. Writing this integral in terms of the standard integral f(x), (equation (5.2.17)) and its derivatives, we get an expression for the dynamic image potential,

$$V(z,v) = -\frac{q^2\omega_s}{2v}\left[f(x) + \lambda\left\{\frac{1}{2} - x\cdot f(x) - \frac{x^2}{2}\frac{df(x)}{dx}\right\}\right]. \quad (5.2.42)$$

This expression also reduces to the expression in the constant speed approximation with v replaced by its local speed, if 'a' is set equal to zero.

The acceleration is obtained in this case also by using the classical equation of motion (5.2.24). Again neglecting variation of 'a' with z as compared to that of v, we obtain,

$$\lambda = \frac{-2\ df/dx}{\frac{q^2\omega_s^2}{2mv^3} - \left\{f(x) + 3x\frac{df(x)}{dx} + x^2\frac{d^2f(x)}{dx^2}\right\}}. \quad (5.2.43)$$

Here too we can solve the energy conservation equation (5.2.18) self-consistently with equations (5.2.42) and (5.2.43) to obtain values of the dynamic image potential. The results obtained in this case as well as in the model Hamiltonian approach are discussed in the next Section.

5.3 RESULTS

We have carried out calculations for V(z,v) in the model Hamiltonian approach for the special case of an electron approaching the metal surface. The dynamic image potential values as a function of z, the distance of the electron from the metal surface are obtained for different electron densities of the metal in the metallic density range (i.e. $1.8 \leq r_s \leq 5.6$) and for different incident energies of the electron. The incident energy ϵ_o of the electron is taken to be of the order of plasmon energy or lower so that for $\epsilon_o = y(\hbar\omega_p)$, $y \leq 1$. Figures (5.1) to (5.11) are the plots of image potential V (in units of ϵ_F, the Fermi energy) against the distance z (in units of a_o , the Bohr radius). In all these figures, curve 1 is the plot for self-consistent local speed calculations[13] and curve 2 corresponds to the calculation incorporating acceleration. Figures (5.1) to (5.4) corresponds to the plots of V(z,v) vs z for r_s = 2,3,4 and 5 respectively, where in all these figures y(the ratio of the incident energy to the plasmon energy) is 0.1. Figures (5.5) to (5.7) correspond to r_s = 3,4 and 5 with y = 0.25 in each of these cases. Similarly, figures (5.8) and (5.9) are for r_s = 4 and 5 with y = 0.5 and figures (5.10) and (5.11) correspond to y = 1.0 for r_s = 4 and 5 again.

The figures (5.1) to (5.4) indicate that the modification in image potential values calculated with acceleration

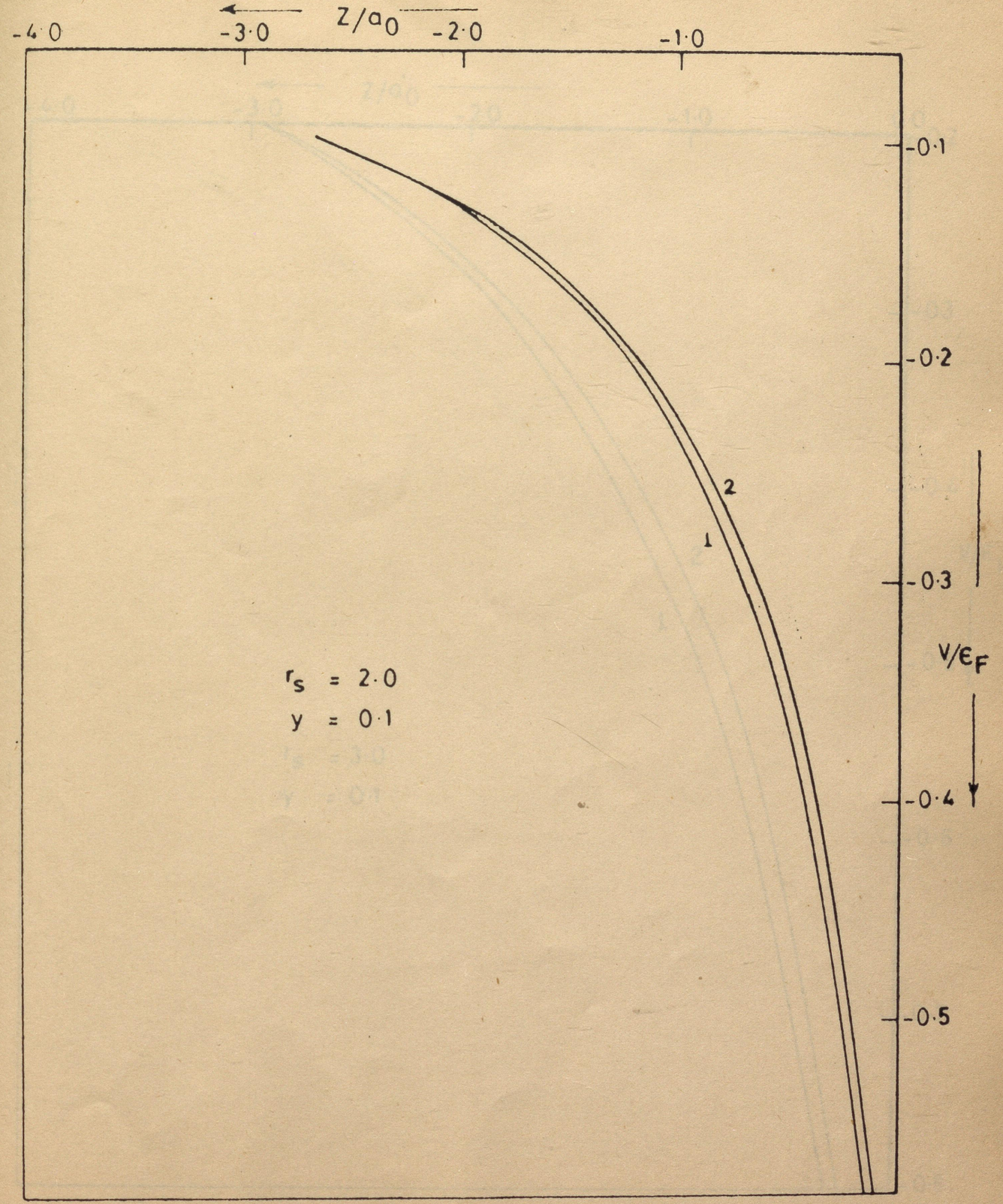


FIG. 5·1

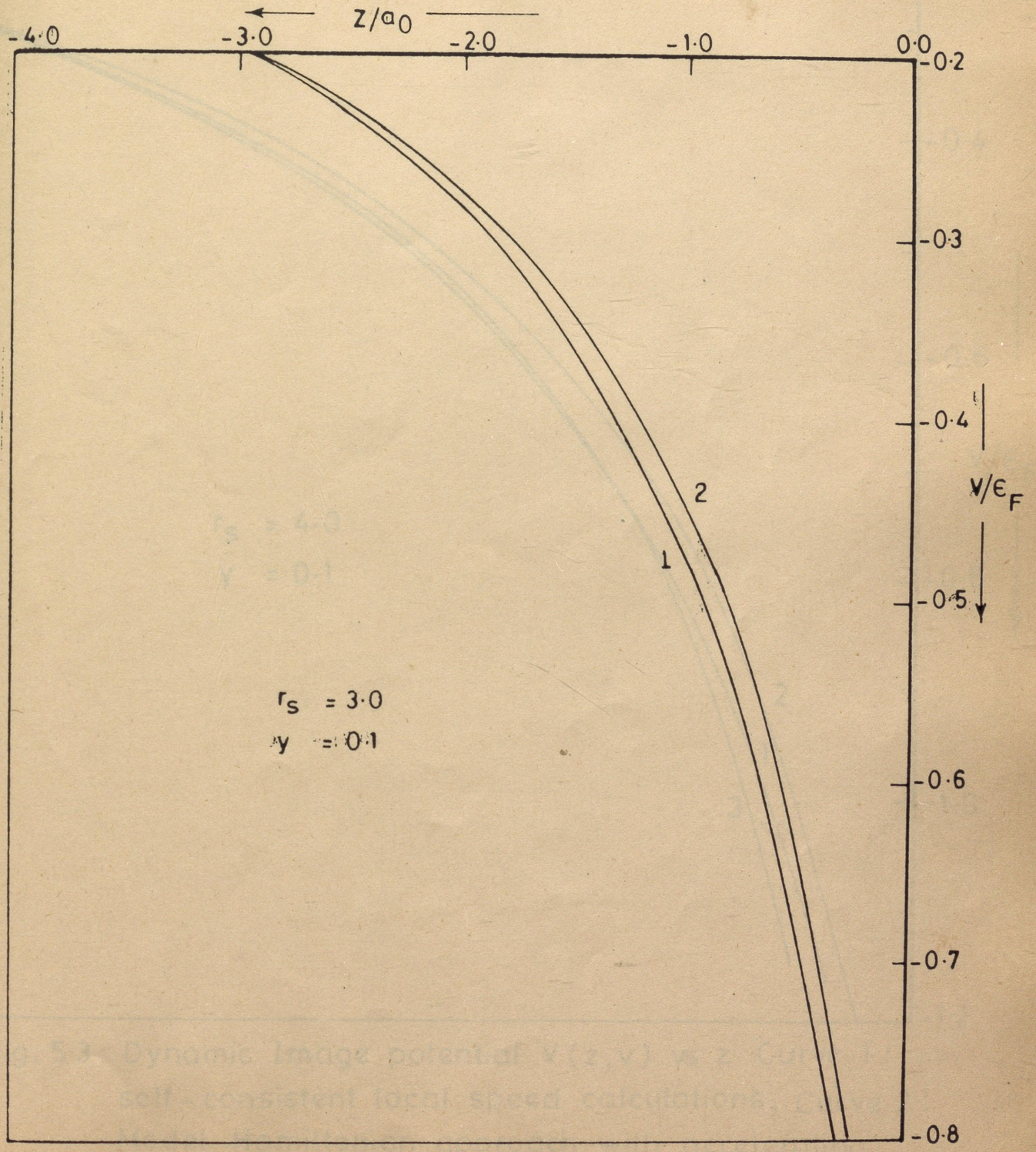


FIG. 5·2

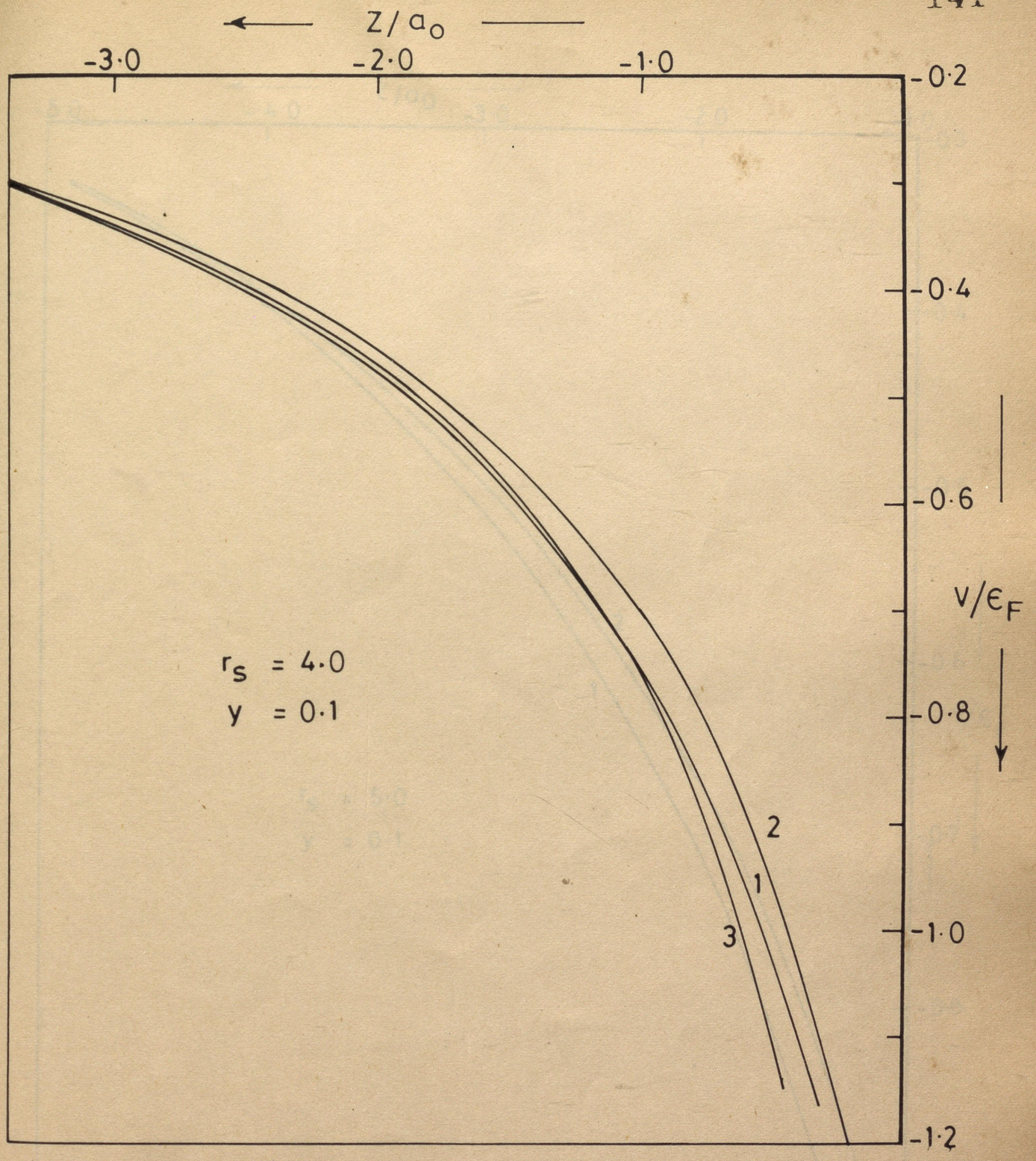


Fig. 5·3: Dynamic Image potential V(z,v) vs z Curve 1: self-consistent local speed calculations; Curve 2: Model Hamiltonian approach with acceleration; Curve 3: Dielectric response approach with acceleration.

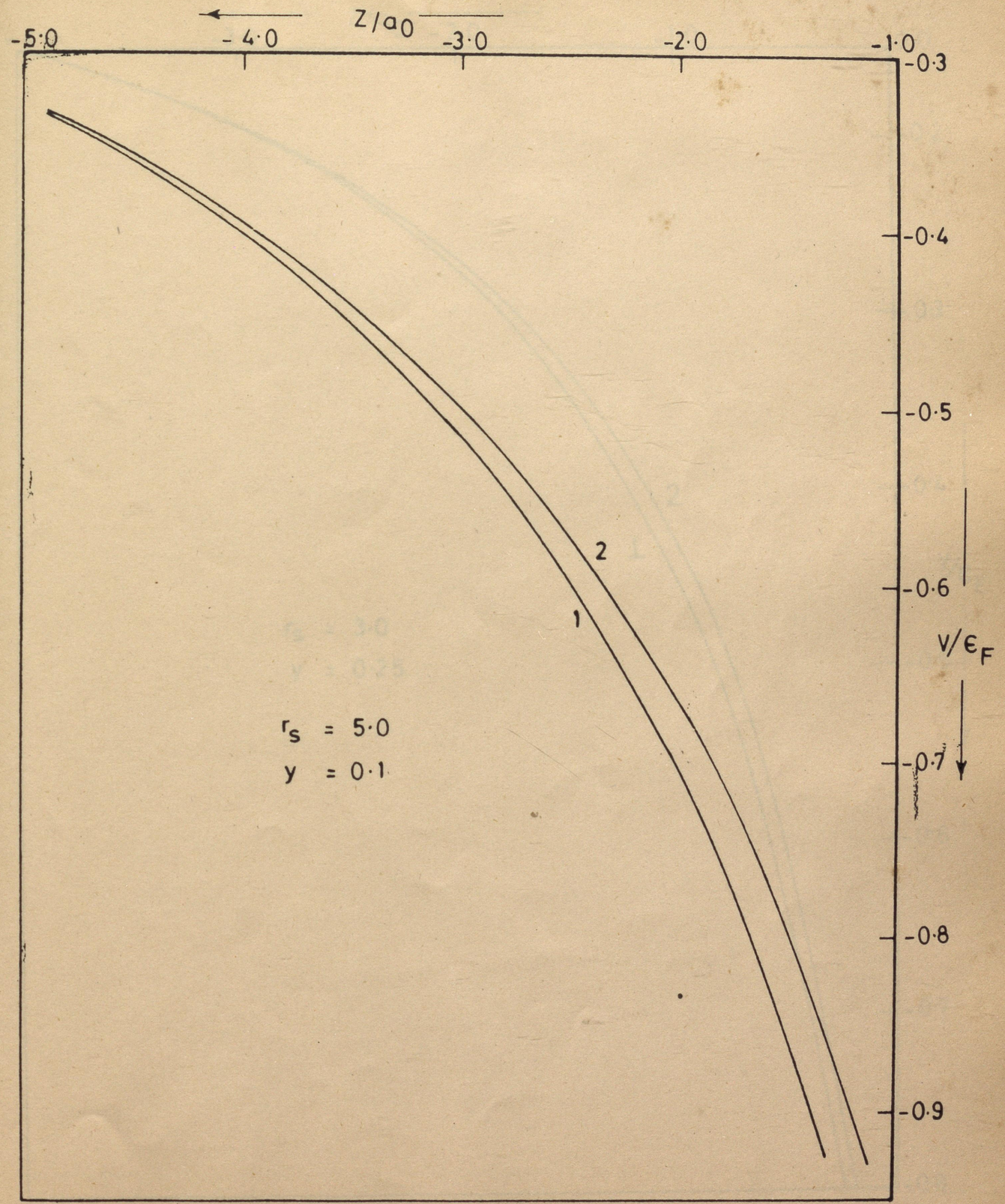


FIG. 5·4

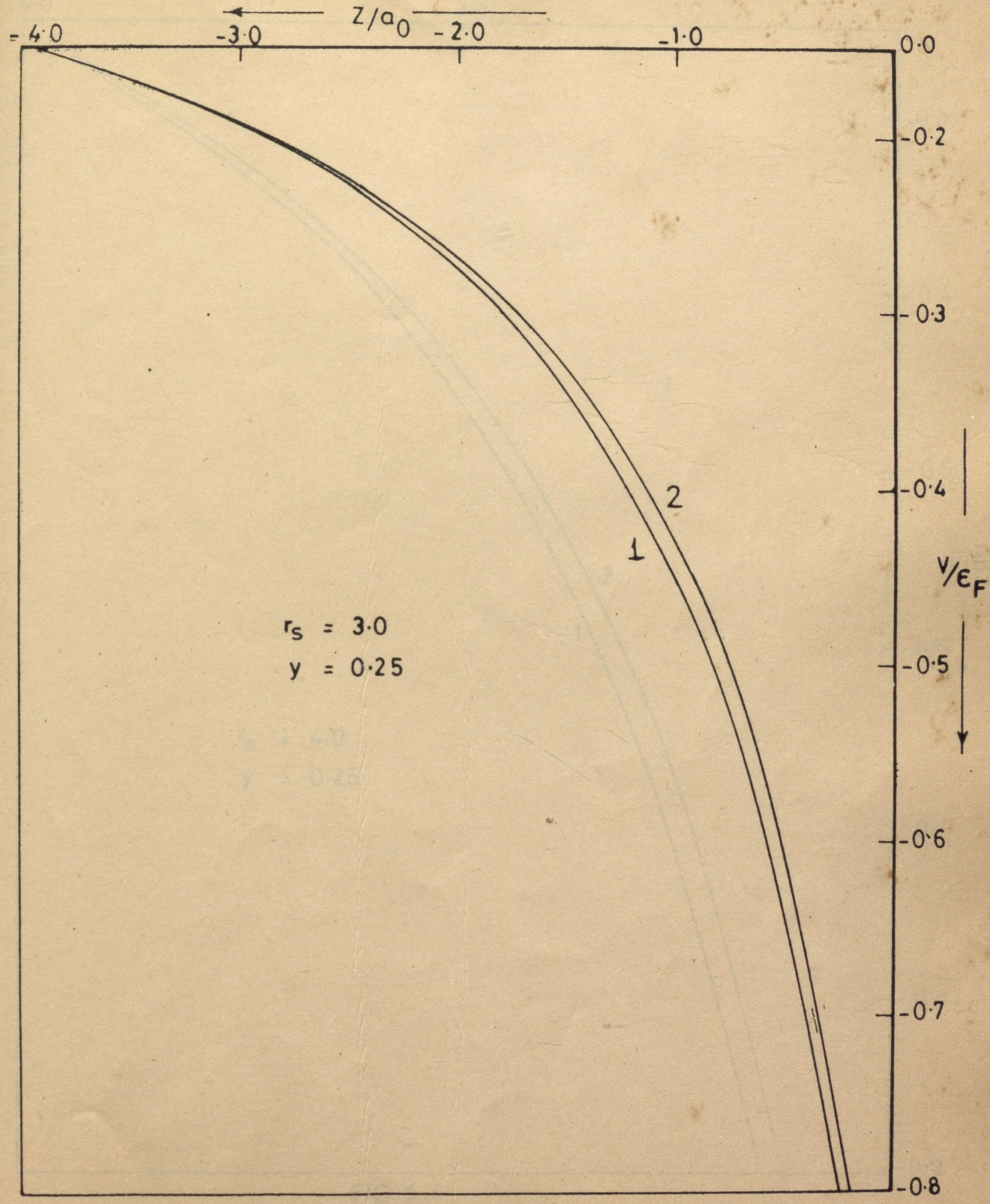


FIG. 5·5

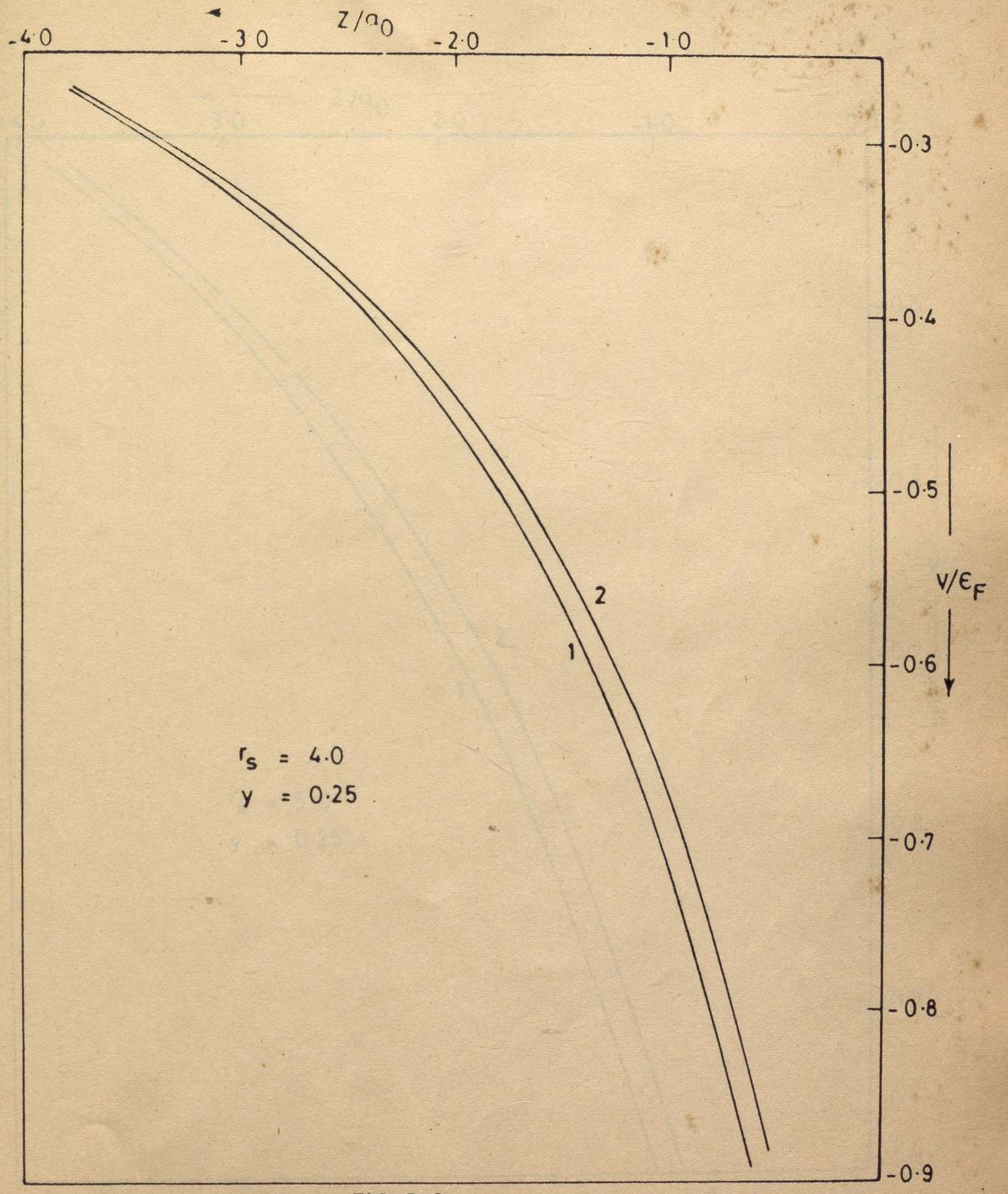


FIG. 5·6

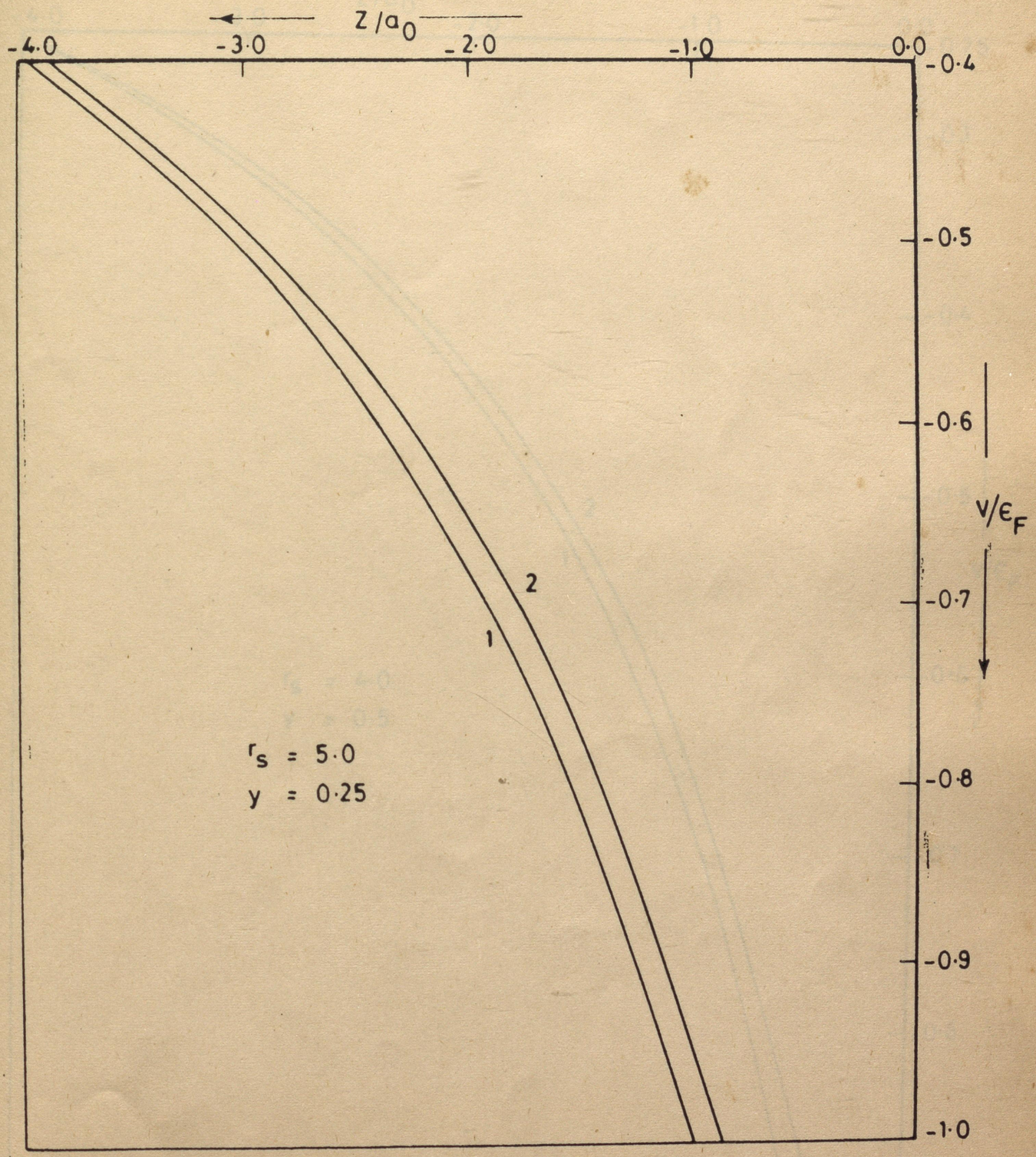


FIG. 5.7

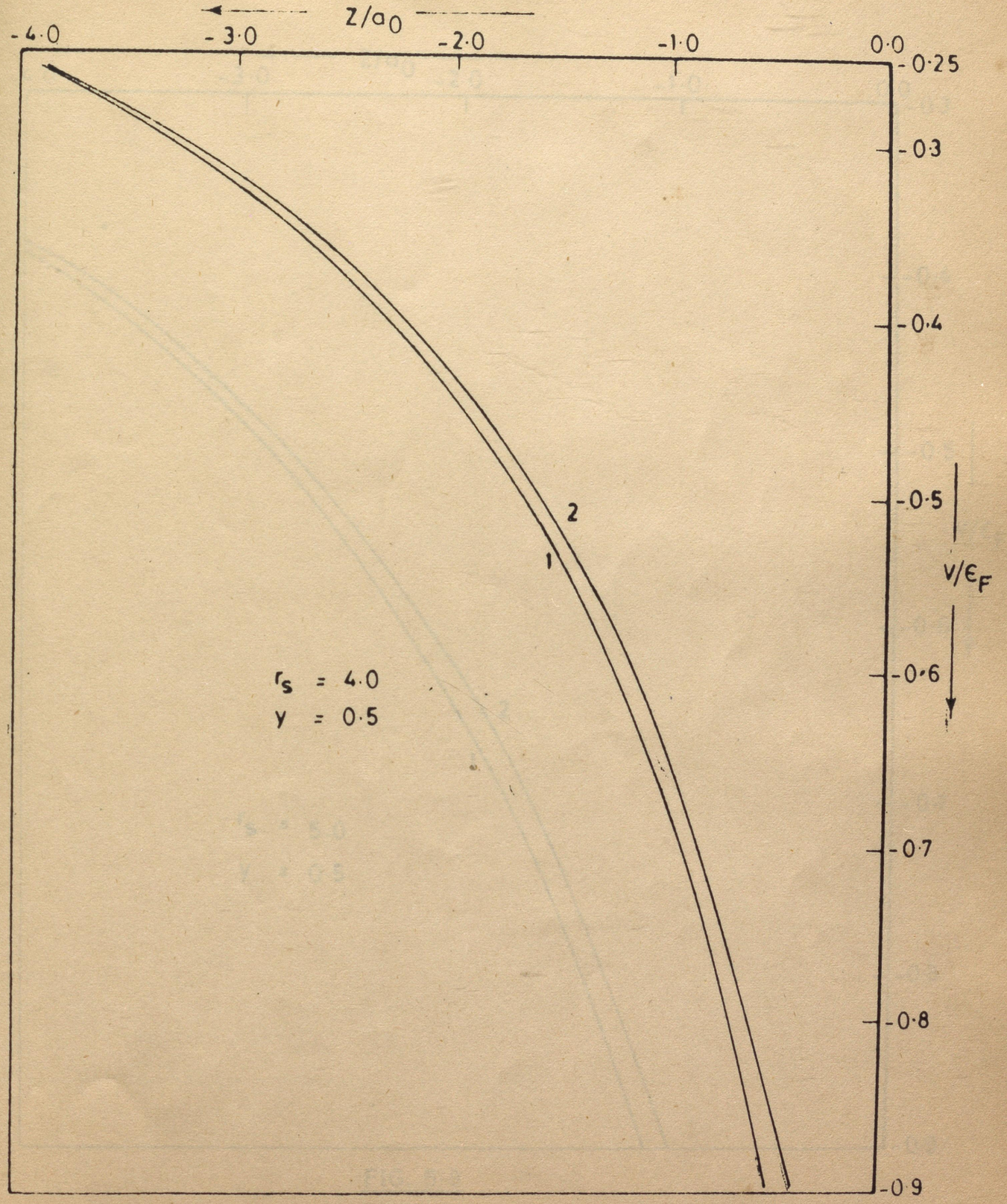


FIG. 5·8

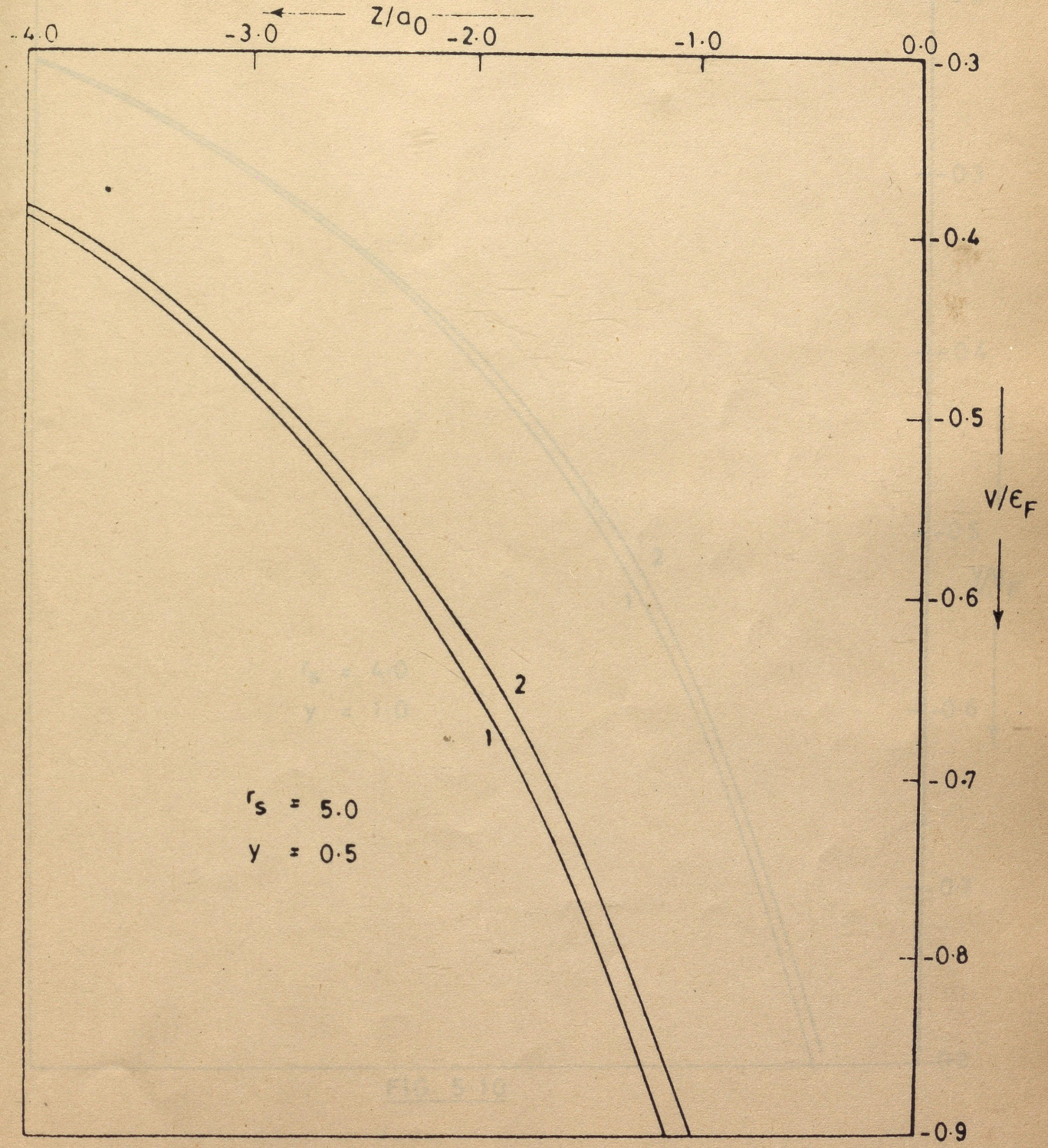


FIG. 5·9

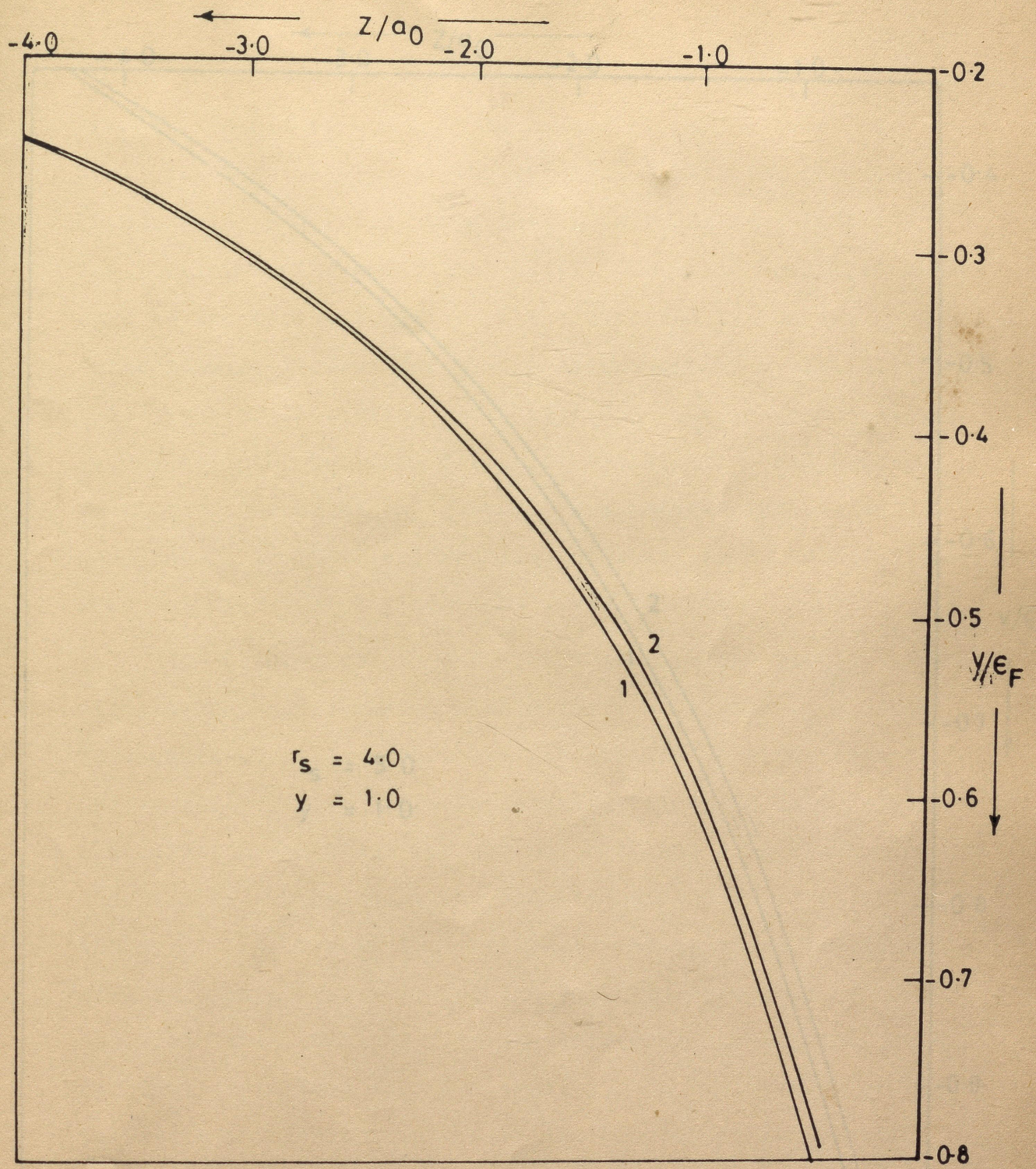


FIG. 5·10

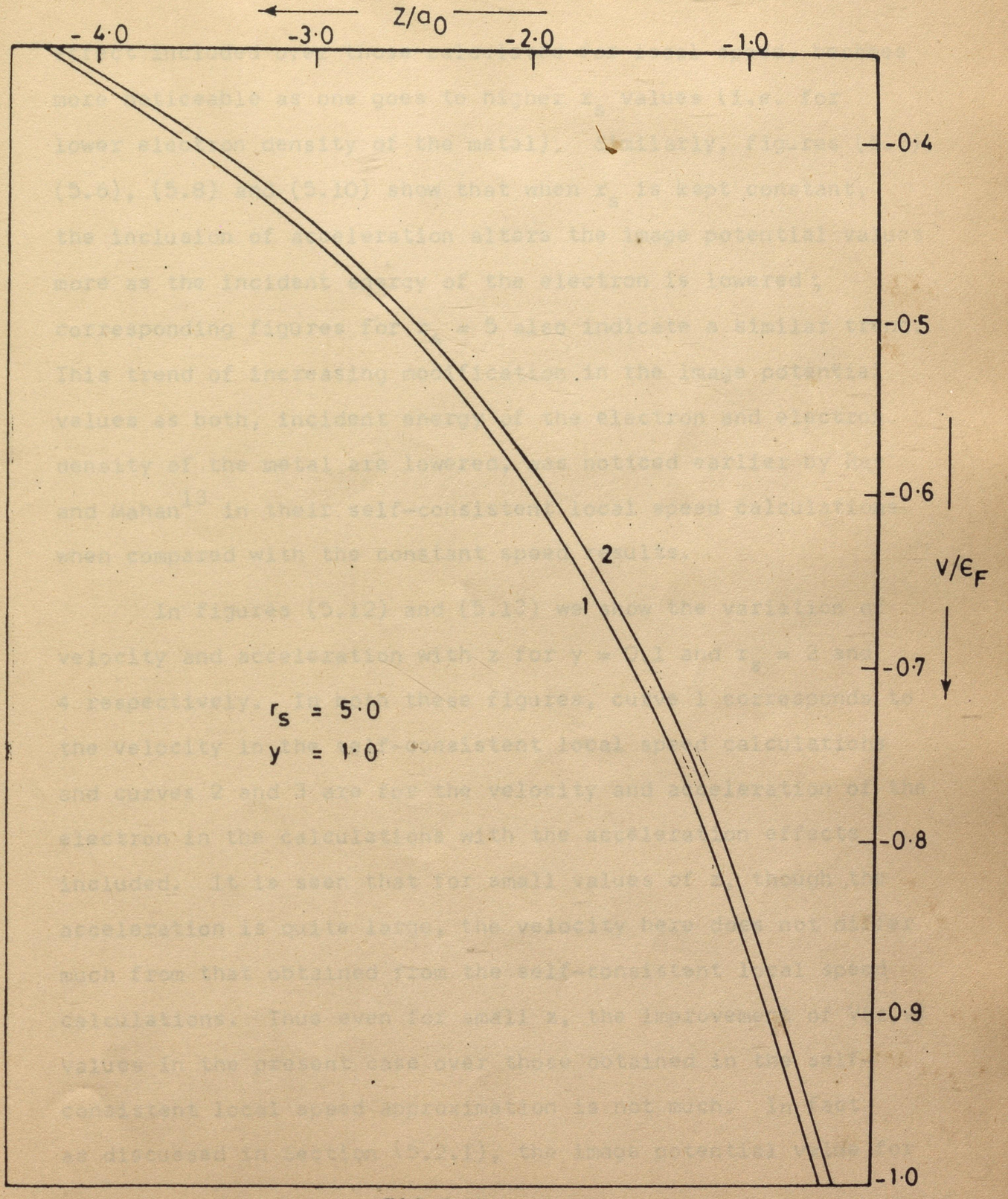


FIG. 5.11

effect included over those calculated for local speed, becomes more noticeable as one goes to higher r_s values (i.e. for lower electron density of the metal). Similarly, figures (5.3), (5.6), (5.8) and (5.10) show that when r_s is kept constant, the inclusion of acceleration alters the image potential values more as the incident energy of the electron is lowered; corresponding figures for $r_s = 5$ also indicate a similar trend. This trend of increasing modification in the image potential values as both, incident energy of the electron and electron density of the metal are lowered, was noticed earlier by Ray and Mahan[13] in their self-consistent local speed calculations when compared with the constant speed results.

In figures (5.12) and (5.13) we show the variation of velocity and acceleration with z for $y = 0.1$ and $r_s = 2$ and 4 respectively. In both these figures, curve 1 corresponds to the velocity in the self-consistent local speed calculations and curves 2 and 3 are for the velocity and acceleration of the electron in the calculations with the acceleration effects included. It is seen that for small values of z, though the acceleration is quite large, the velocity here does not differ much from that obtained from the self-consistent local speed calculations. Thus even for small z, the improvement of $V(z,v)$ values in the present case over those obtained in the self-consistent local speed approximation is not much. In fact as discussed in Section (5.2.1), the image potential value for

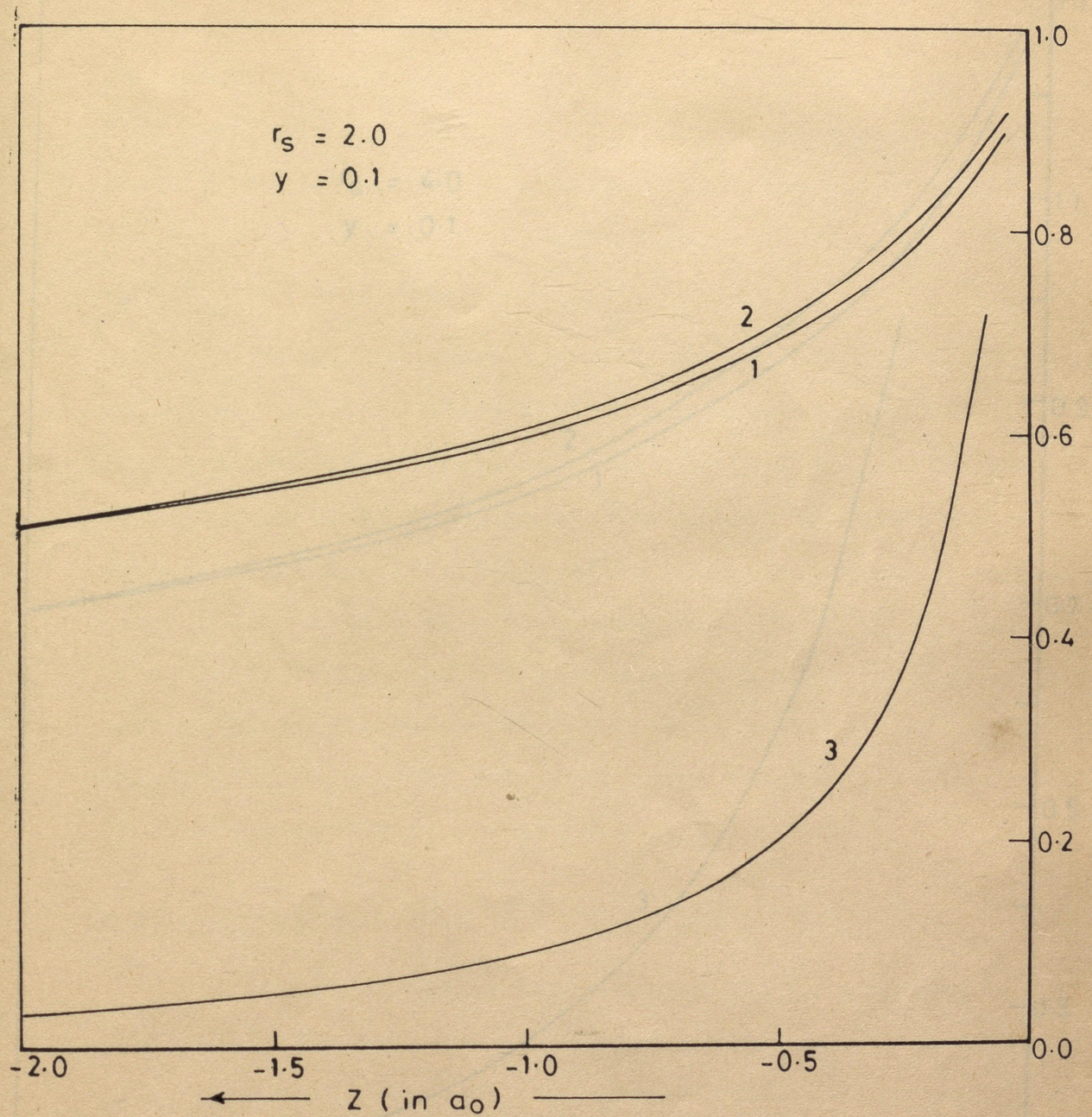


Fig. 5.12 Curve 1: Velocity calculated in self consistent local speed calculations; Curve 2 and 3: Velocity and acceleration in calculations taking acceleration into account

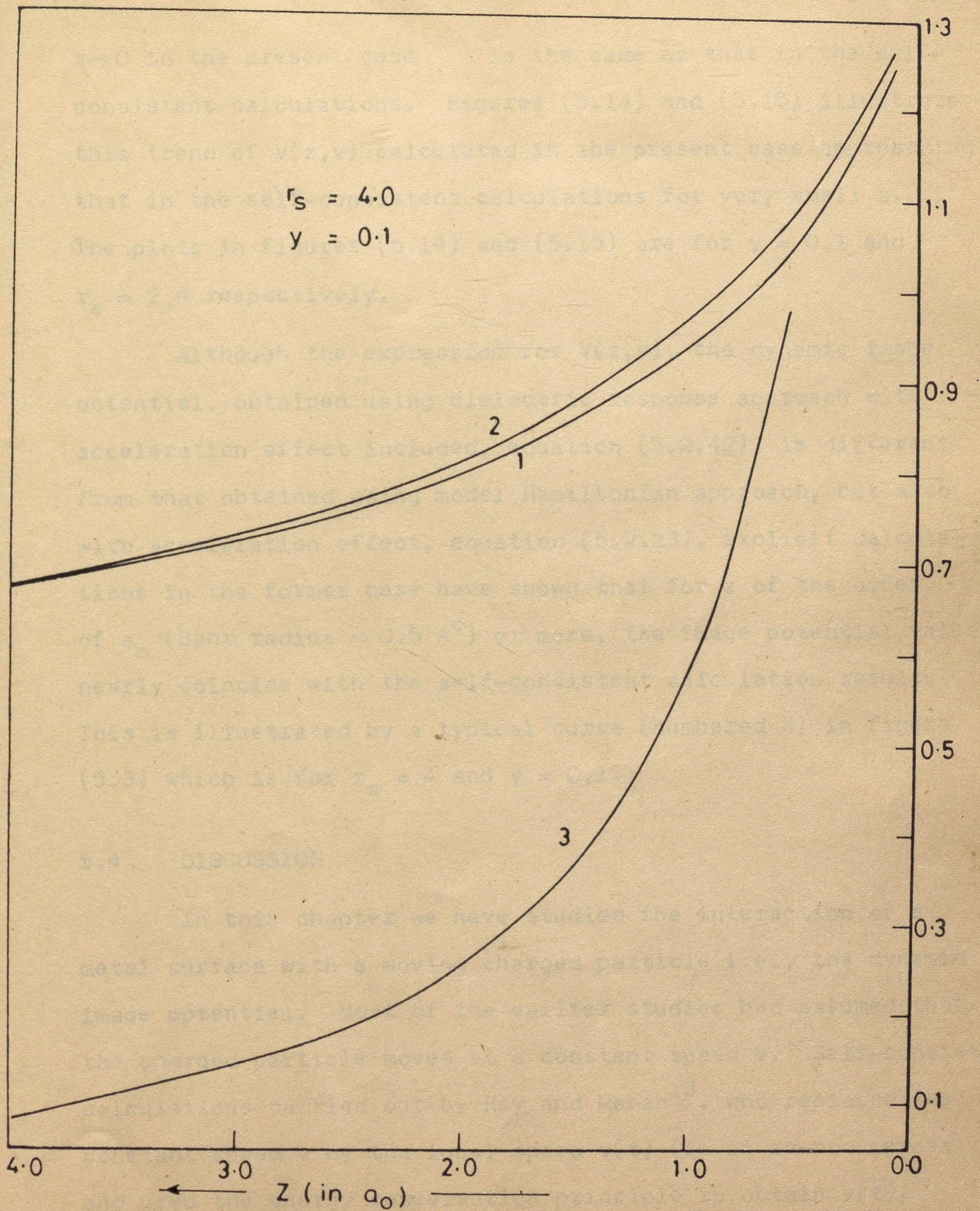


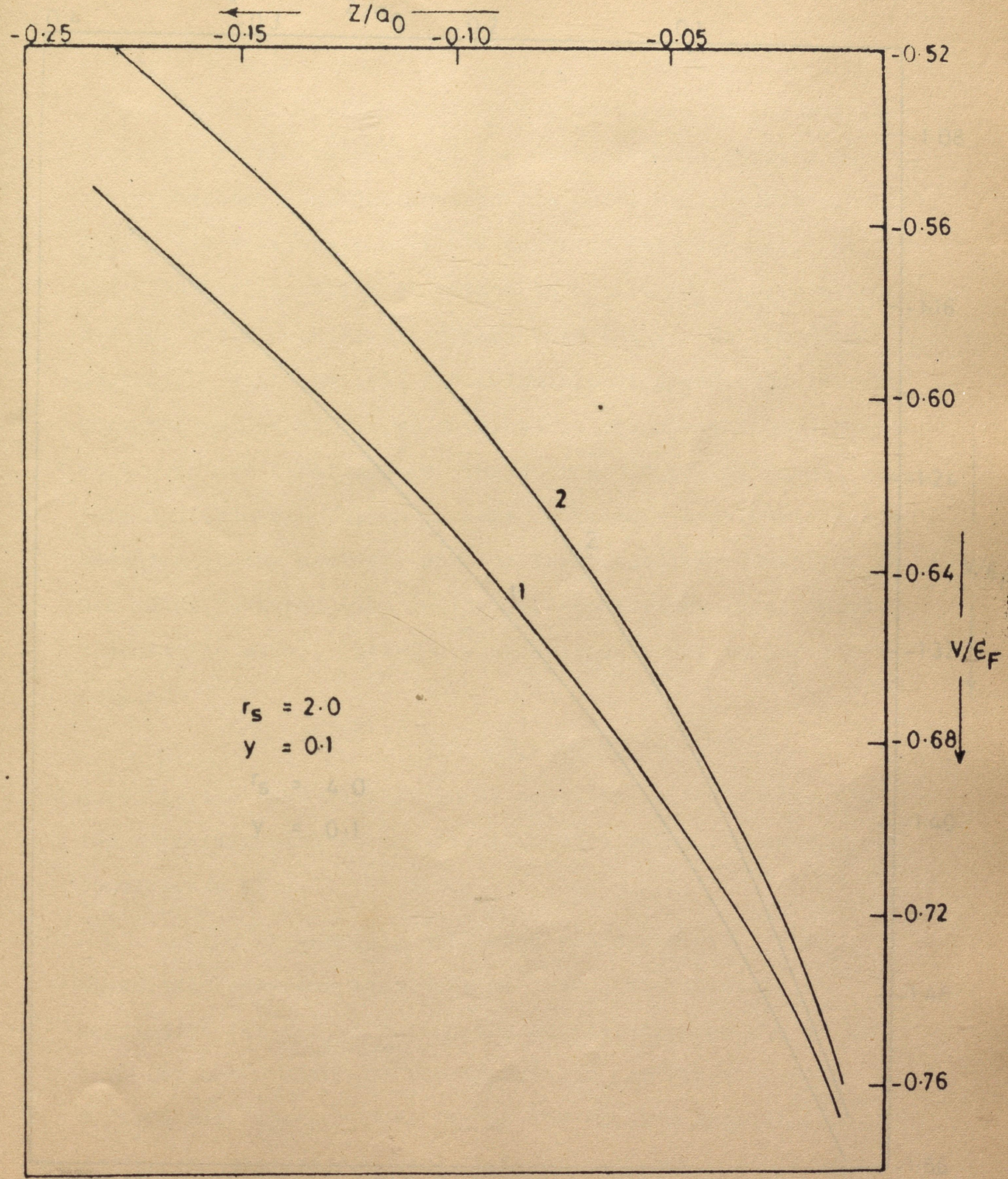
Fig. 5·13 Curve 1: Velocity calculated in self consistent local speed calculations; Curve 2 and 3: Velocity and acceleration in calculations taking accelera-tion into account

$z \to 0$ in the present case is the same as that in the self-consistent calculations. Figures (5.14) and (5.15) illustrate this trend of $V(z,v)$ calculated in the present case approaching that in the self-consistent calculations for very small z. The plots in figures (5.14) and (5.15) are for $y = 0.1$ and $r_s = 2,4$ respectively.

Although the expression for $V(z,v)$, the dynamic image potential, obtained using dielectric response approach with acceleration effect included, equation (5.2.42), is different from that obtained using model Hamiltonian approach, but also with acceleration effect, equation (5.2.23), explicit calculations in the former case have shown that for z of the order of a_o (Bohr radius ~ 0.5 A^o) or more, the image potential values nearly coincide with the self-consistent calculation results. This is illustrated by a typical curve (numbered 3) in figure (5.3) which is for $r_s = 4$ and $y = 0.1$.

5.4 DISCUSSION

In this chapter we have studied the interaction of a metal surface with a moving charged particle i.e., the dynamic image potential. Most of the earlier studies had assumed that the charged particle moved at a constant speed v. Self-consistent calculations carried out by Ray and Mahan[13], who replaced the constant speed v by the local speed $v(t)$ (in an ad-hoc manner) and used the energy conservation principle to obtain $v(t)$,



FIG·5.14

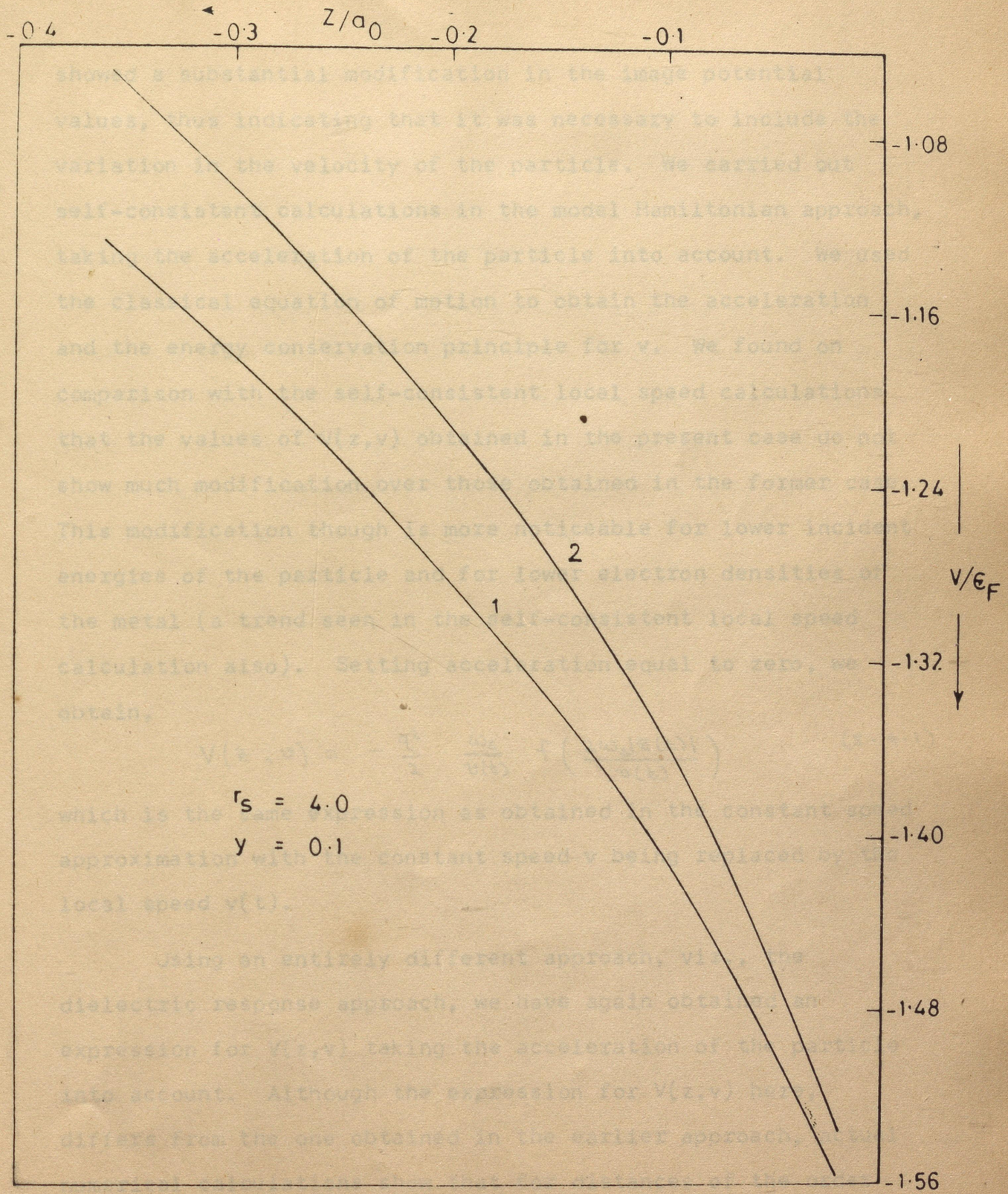


FIG. 5·15

showed a substantial modification in the image potential values, thus indicating that it was necessary to include the variation in the velocity of the particle. We carried out self-consistent calculations in the model Hamiltonian approach, taking the acceleration of the particle into account. We used the classical equation of motion to obtain the acceleration and the energy conservation principle for v. We found on comparison with the self-consistent local speed calculations that the values of V(z,v) obtained in the present case do not show much modification over those obtained in the former case. This modification though is more noticeable for lower incident energies of the particle and for lower electron densities of the metal (a trend seen in the self-consistent local speed calculation also). Setting acceleration equal to zero, we obtain,

$$V(z,v) = -\frac{q^2}{2} \cdot \frac{\omega_s}{v(t)} \cdot f\left(\frac{2\omega_s|z(t)|}{v(t)}\right) \qquad (5.4.1)$$

which is the same expression as obtained in the constant speed approximation with the constant speed v being replaced by the local speed v(t).

Using an entirely different approach, viz., the dielectric response approach, we have again obtained an expression for V(z,v) taking the acceleration of the particle into account. Although the expression for V(z,v) here, differs from the one obtained in the earlier approach, actual numerical calculations show that for distances of the order

of a_o (Bohr radius) and above, numerical V(z,v) values calculated in this case coincide with the self-consistent local speed calculations. In this case too, on setting the acceleration equal to zero we get equation (5.4.1), showing how the local speed of the particle enters the self-consistent theory.

Thus in both the approaches we do not see any significant modification in V(z,v) as compared to the self-consistent local speed calculations. However, due to the inclusion of local speed in the theory in a natural way, we are able to provide a mathematical justification to the use of the simpler self-consistent local speed calculations[13].

CHAPTER 6

DYNAMIC INTERACTION BETWEEN ATOM OR MOLECULE AND A METALLIC SURFACE

The atom and molecular beam scattering[14,83,84] and the adsorption experiments[15] on metal surfaces have revived interests in van der Waals interaction, which forms the attractive part of the interaction between a neutral atom or molecule and a metal surface. The surprisingly significant discrepancy[14] between experiment and theory for this coupling, has initiated a lot of theoretical work in this field[16,85-87]. Here we study the effect of the velocity of the atom or molecule on this interaction, again mainly in the model Hamiltonian approach. We also study the interaction of a neutral atom or molecule with adsorbed molecules.

Section (6.1) of this chapter deals with the dynamic interaction (van der Waals type) between a moving atom or molecule and a planar, metal surface calculated using both, the model Hamiltonian and dielectric response approach. In Section (6.2), we calculate the single loss probability for an atom or molecule approaching a metal surface having an uniform layer of adsorbed molecules. We end the chapter with a brief discussion in Section (6.3).

6.1 DYNAMIC VAN DER WAALS INTERACTION BETWEEN AN ATOM OR MOLECULE AND A METALLIC SURFACE

The interaction between an atom and a metal is a combination of two potentials; the long ranged attractive polarisation potential and the short ranged repulsive potential arising from the overlap of the electronic clouds of the atom and the metal surface. In a series of atom and molecular scattering experiments[14,83,84], the attractive potentials (which reduce to the dispersive van der Waals (vdW) interaction, if the atom or molecule has negligible permanent dipole moment[88]) between atomic or molecular dipoles and metallic surfaces have been studied. Surprisingly one finds a significant discrepancy between theory and experiment, for the strength of the coupling ; the experimental result being about 60% less than the predicted theoretical values[14]. There exists extensive literature on the subject[16,85-87].

In the non-retarded limit, the attractive interaction between a planar metal surface and a dipole placed at a distance z from the surface, is proportional to $|z|^{-3}$ for large separation z. Most of the theoretical work has been concentrated on getting corrections to the $|z|^{-3}$ term in the smaller z-regime. Seeing the effect of the dynamics of the particle on the image potential values, we attempt to study here the modification to dipole-metal interaction in the non-retarded limit, due to the inclusion of the velocity of the incoming atom or molecule.

6.1.1 Model Hamiltonian approach

In this study we assume that the neutral atom or molecule is represented by a point dipole of effective charge e_o and mass m_o. The interaction between the surface plasmons of the metal and the dipole can be approximated by a model Hamiltonian which can be obtained from equation (5.2.2) :

$$H_I = \sum_{\underset{\sim}{k}} \Gamma_{\underset{\sim}{k}} \, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\xi}} \, e^{-k|z|} \, (a_{\underset{\sim}{k}} + a^{+}_{\underset{\sim}{k}}) \left(\frac{\hbar}{2m_o\omega_o}\right)^{1/2}, \qquad (6.1.1)$$

where, $(\hbar e_o^2/2m_o\omega_o)^{1/2}$ is the dipole moment of the molecule and Γ_k is the same coupling constant as defined in (5.2.3). Again assuming the same geometry of the system as before, i.e., metal in $z > 0$ region with surface in x-y plane at $z = 0$ and the dipole approaching the surface along the z-axis from the $z < 0$ region, in the interaction representation we have the time development of the wave-function for the system given by,

$$\psi(t) = \exp\left[-i \sum_{\underset{\sim}{k}} \left\{ I'_{\underset{\sim}{k}}(t)\, a_{\underset{\sim}{k}} + I'^{*}_{\underset{\sim}{k}}(t)\, a^{+}_{\underset{\sim}{k}} \right\}\right] \psi(-\infty), \qquad (6.1.2)$$

where,

$$I'_{\underset{\sim}{k}}(t) = k\Gamma_k \int_{-\infty}^{t} dt' \; e^{kz(t') + i\omega_s t'} \left(\frac{\hbar}{2m_o\omega_o}\right)^{1/2}. \qquad (6.1.3)$$

Assuming that the incoming particle is moving at a constant speed v, we can replace $z(t) = vt$, so that,

$$I'_k(t) = k\Gamma_k \left(\frac{\hbar}{2m_o\omega_o}\right)^{1/2} \frac{e^{i\omega_s t + kvt}}{kv + i\omega_s}.$$

We proceed in exactly the same manner as in section (5.2.1) for dynamic image potential. Identifying the expectation value of the Hamiltonian given in equation (5.2.4) with the induced self energy of the neutral particle or the dynamic vdW

interaction W(z,v), we obtain,

$$W(z,v) = -\sum_k \hbar\omega_s |I'_k(t)|^2 \quad , \tag{6.1.4}$$

$$= -\frac{\pi e_o^2 \omega_s^2}{2m_o\omega_o} \cdot \frac{1}{2\pi} \int_0^\infty dk \cdot k^2 \frac{e^{2kz}}{k^2v^2+\omega_s^2} \, ,$$

$$= -\frac{\langle r^2\rangle}{3} \int_0^\infty dk \; k^2 \cdot \frac{e^{-2k|z|}}{k^2v^2/\omega_s^2+1} \quad . \tag{6.1.5}$$

To write (6.15) we have used the relation between the oscillator strength $f_o = e_o^2/2m_o$ of the dipole and $\langle r^2\rangle$, viz.,

$$\frac{f_o}{\omega_o} = \frac{2}{3}\langle r^2\rangle \quad . \tag{6.1.6}$$

Writing equation (6.1.5) in terms of the function f(x), defined in equation (5.2.17), we have ,

$$W(z,v) = -\frac{\langle r^2\rangle}{12}\left(\frac{\omega_s}{v}\right)^3 4 \cdot \frac{d^2f(x)}{dx^2} \quad . \tag{6.1.7}$$

To our knowledge this result for dynamic vdW interaction is new. To relate this expression to the classical result for a static particle, we set v = 0 in equation (6.1.5),

$$W(z, v=0) = -\frac{\langle r^2\rangle}{3} \int_0^\infty dk \cdot k^2 \cdot e^{-2k|z|} \, ,$$

$$= -\frac{\langle r^2\rangle}{12} \cdot \frac{1}{|z|^3} \quad . \tag{6.1.8}$$

The ratio of the dynamic and static vdW interaction is then given by,

$$\frac{W(z,v)}{W(z,v=0)} = \frac{1}{2} x^3 \cdot \frac{d^2f(x)}{dx^2} \quad . \tag{6.1.9}$$

Using the large x expansion for f(x)[79],

$$f(x) \longrightarrow \frac{1}{x}\left(1 - \frac{2!}{x^2} + \frac{4!}{x^4} - \frac{6!}{x^6} + \cdots\right),$$

the large x or equivalently the large z expansion for W(z,v) is,

$$W(z,v) \longrightarrow -\frac{\langle r^2\rangle}{12} \cdot \frac{1}{|z|^3}\left(1 - \frac{3v^2}{\omega_s^2} \cdot \frac{1}{|z|^2} + \cdots\right). \tag{6.1.10}$$

The second term in (6.1.10) is then the dynamic correction to the static result in large z-regime.

For large x, the R.H.S. of equation (6.1.9) approaches unity giving no significant correction over the static W value. We find that due to the large mass of the incoming particle, its velocity v is very small thus giving for any significant value of z (which would be of the order of at least a few atomic units), a very large value of x and hence a negligible dynamic correction. Even a self-consistent calculation, along the lines considered and discussed for dynamic image potential in Section (5.2), does not give any measurable dynamic corrections to the vdW interaction. Iterations for the local speed using energy conservation principle fail to give v of such a magnitude that x could be lowered to values giving non-vanishing dynamical correction to the static van der Waals interaction.

6.1.2 Response function approach

It is instructive to study the dynamic vdW starting from the dielectric response approach. For a charge $q(t) = q(\omega_o)e^{i\omega_o t}$ approaching a metal surface, the potential due to the charge density induced in the metal by this charge, at the location r(t) of the charge is given in equation (5.2.38). If we assume that the charge q(t) moves at a constant velocity $\underset{\sim}{v}$, the following expansions are valid :

$$z(t') = z(t - t_1) = z(t) - v_\perp t_1 \quad ; \qquad (6.1.11)$$

and $$\underset{\sim}{s}(t') = \underset{\sim}{s}(t - t_1) = \underset{\sim}{s}(t) - \underset{\sim}{v}_{\parallel} t_1 \ .$$

Substituting these in equation (5.2.34) and using the classical form, equation (5.2.40) for the form factor, we have,

$$V_i(\underset{\sim}{r}(t)) = q(\omega_0)\int \frac{d^2k}{(2\pi)^2}\cdot\frac{2\pi}{k}\, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}-\underset{\sim}{\rho}_0(t))}\, e^{kz+kz_0(t)}\cdot\frac{\omega_s^2}{(\omega_0+\underset{\sim}{k}\cdot\underset{\sim}{v}_{11}+ikv_\perp)^2-\omega_s^2}\quad .\quad (6.1.12)$$

We consider a dipole of constant strength $\underset{\sim}{\mu} = 2q\underset{\sim}{d}$ (i.e. $q(t)=q$) approaching the metal surface along the z axis. The point dipole approximation is used according to which, for $q\to\infty$ and $d\to 0$, $2q\underset{\sim}{d}$ is equal to the finite quantity $\underset{\sim}{\mu}$. In this case the total induced potential at point $\underset{\sim}{r} \equiv (\underset{\sim}{\rho}, z)$ is,

$$V_i(\underset{\sim}{r}(t)) = \int \frac{d^2k}{(2\pi)^2}\cdot\frac{2\pi}{k}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}+kz}\cdot\frac{q\,\omega_s^2}{(\underset{\sim}{k}\cdot\underset{\sim}{v}_{11}+ikv_\perp)^2-\omega_s^2}$$

$$\cdot\left[e^{-i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}_0(t)+\underset{\sim}{d})+k(z_0(t)+d_z)} - e^{-i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}_0(t)-\underset{\sim}{d})+k(z_0(t)-d_z)}\right],$$

$$= 2q\omega_s^2\int\frac{d^2k}{2\pi k}\,\frac{e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\rho}-\underset{\sim}{\rho}_0(t))+k(z+z_0(t))}}{(\underset{\sim}{k}\cdot\underset{\sim}{v}_{11}+ikv_\perp)^2-\omega_s^2}\,(kd_z - i\underset{\sim}{k}\cdot\underset{\sim}{d})\quad .\quad (6.1.13)$$

If we take $\underset{\sim}{v}_{11} = 0$ and assume that the dipole apporaches the surface along z-axis, the field at $\underset{\sim}{r}_0(t) = (0,0,z_0(t))$ i.e. at the incoming dipole due to this induced potential is given by,

$$E_i(\underset{\sim}{r}_0(t)) = -\nabla_i V_i(\underset{\sim}{r}_0(t))\quad .$$

$$\text{So,}\quad E_z(\underset{\sim}{r}_0(t)) = 2q\omega_s^2\int\frac{d^2k}{2\pi k}\,\frac{e^{2kz_0(t)}}{k^2v_\perp^2+\omega_s^2}\,k(kd_z - i\underset{\sim}{k}\cdot\underset{\sim}{d}),$$

$$= \mu_z\cdot I\quad . \qquad (6.1.14)$$

where
$$I = \omega_s^2\int_0^\infty dk\,\frac{k^2\cdot e^{2kz_0(t)}}{k^2v_\perp^2+\omega_s^2}\quad . \qquad (6.1.15)$$

Similarly we have,

$$E_x(\underset{\sim}{r}_0(t)) = 2qd_x\omega_s^2\int\frac{d^2k}{2\pi k}\cdot\frac{e^{2kz_0(t)}}{k^2v_\perp^2+\omega_s^2}\,k_x^2,$$

$$= \frac{1}{2}\mu_x I$$

and $$E_y(\underset{\sim}{r}_o(t)) = \tfrac{1}{2}\mu_y I \ .$$

because averaging over θ gives $\langle k_x^2\rangle_\theta = \langle k_y^2\rangle_\theta = \frac{1}{2}k^2$.
The interaction energy or electrostatic self energy of the incoming dipole is , then,

$$W(z,v) = -\tfrac{1}{2}\underset{\sim}{\mu}\cdot\underset{\sim}{E}(\underset{\sim}{r}_o(t)),$$

$$= -\tfrac{1}{2}\left[\frac{\mu_x^2}{2} + \frac{\mu_y^2}{2} + \mu_z^2\right] I .$$

Since there is no preferential orientation for the dipole one must average over all possible orientations of the dipole. The average interaction energy is then,

$$W(z_o,v) = -\frac{\mu^2}{3}\omega_s^2 \int_0^\infty dk\, k^2 \frac{e^{2kz_o}}{k^2v^2+\omega_s^2} \ . \qquad (6.1.16)$$

where we use the fact that when averaged $\mu_x^2 = \mu_y^2 = \mu_z^2 = \frac{\mu^2}{3}$.
In the static case this reduces to $W(z_o, v=0) = -\frac{\mu^2}{12}\frac{1}{|z_o|^3}$.
This is the expression used for the strength of the interaction in the experimental work by Shih and Parsegian[14].

If the atom or molecule has no permanent dipole moment then μ is entirely due to induced dipole moment, in which case, one replaces μ^2 above by $\langle r^2\rangle$ (in atomic units), which gives the usual classical result (6.1.6). It however does not contain any effect due to the internal structure in case of induced dipole moment. This can be incorporated easily through the method of fluctuations. In case $\underset{\sim}{\mu}(t)$ is a fluctuating dipole we take $q(t) = q(\omega_o)e^{i\omega_o t}$ so that $\underset{\sim}{\mu}(t) = \underset{\sim}{\mu}(\omega_o)e^{i\omega_o t}$. Then for $\underset{\sim}{v}_{\parallel} = 0$, writing $E_i(t) = E_i(\omega_o)e^{i\omega_o t}$ etc., we have from equation (6.1.14),

$$E_z(\omega_0) = \mu_z(\omega_0)\, J(\omega_0) \qquad (6.1.17)$$

where, $$J(\omega_0) = \omega_s^2 \int_0^\infty dk\, \frac{k^2 \cdot e^{2kz}}{(kv - i\omega_0)^2 + \omega_s^2} \,. \qquad (6.1.18)$$

Similarly we have,

$$E_{x,y}(\omega_0) = \mu_{x,y}(\omega_0)\, \tfrac{1}{2} J(\omega_0) \,.$$

If the fluctuating dipole is the induced dipole due to the field $\underset{\sim}{E}$ itself, then,

$$\underset{\sim}{\mu}(\omega_0) = \underset{\approx}{\alpha}(\omega_0)\, \underset{\sim}{E}(\omega_0)$$

i.e. $$\mu_i(\omega_0) = \alpha_{ij}(\omega_0) E_j(\omega_0) \,, \qquad (6.1.19)$$

where $\alpha(\omega_0)$ is the dipolar polarisability of the atom or molecule. This implies that,

$$E_i(\omega_0) = \sum_{j=x,y,z} G_{ij}(\omega_0)\, E_j(\omega_0) \,, \quad i = x,y,z \qquad (6.1.20)$$

where,

$$G_{xj} = \alpha_{xj}(\omega_0) \cdot \tfrac{1}{2} J(\omega_0) \,,$$

$$G_{yj} = \alpha_{yj}(\omega_0) \cdot \tfrac{1}{2} J(\omega_0) \,,$$

and $$G_{zj} = \alpha_{zj}(\omega_0)\, J(\omega_0) \,.$$

The equations (6.1.20) are linear homogeneous equations and admit non-trivial solution, only if the determinant

$$D(\omega) = \det |\delta_{ij} - G_{ij}(\omega)| \qquad (6.1.21)$$

vanishes for certain ω values, which are the eigenmodes of the electromagnetic fluctuations for the coupled atom-metal system. For an atom with spherical symmetry in its ground state, $\alpha_{ij}(\omega) = 0$ for $i \neq j$; also let $\alpha_{ii}(\omega) = \alpha_a(\omega)$. Then in this case $G_{ij}(\omega) = 0$ for $i \neq j$ and,

$$2G_{xx}(\omega) = 2G_{yy}(\omega) = G_{zz}(\omega) = \alpha_a(\omega)\, J(\omega) \,.$$

The vdW interaction is then given by

$$W = \frac{1}{2} \sum_i \hbar\omega_i \quad , \tag{6.1.22}$$

where ω_i are the roots of the equation $D(\omega) = 0$. This can be rewritten as,

$$W = \frac{\hbar}{4\pi i} \oint d\omega \cdot \omega \frac{d}{d\omega} \ln D(\omega) \, ,$$

$$= -\frac{\hbar}{4\pi} \int_{-\infty}^{\infty} d\xi \sum_i G_{ii}(i\xi) \, , \quad (\text{if } |G_{ij}| << 1)$$

$$= -\frac{\hbar}{2\pi} \int d\xi \; \alpha_a(i\xi) \, I(i\xi) \, . \tag{6.1.23}$$

For $\alpha_a(\omega)$ we take the form,

$$\alpha_a(\omega) = \sum_n \frac{f_n}{\omega_n^2 - \omega^2} \, . \tag{6.1.24}$$

Then,

$$W = -\hbar\omega_s^2 \sum_n f_n \int_0^\infty dk \cdot k^2 \, e^{2kz_0} \int_{-\infty}^{\infty} \frac{d\xi}{2\pi} \frac{1}{(\omega_n^2 + \xi^2)\left((kv + \xi)^2 + \omega_s^2\right)} \, .$$

The ξ integral is performed in the complex ξ plane by the method of contour integration, to get (in atomic units),

$$W = -\frac{1}{2} \sum_n \frac{f_n}{\omega_n} \int_0^\infty dk \; \frac{k^2 \cdot e^{2kz_0} \left(1 + \omega_n/\omega_s\right)}{k^2 v^2/\omega_s^2 + \left(1 + \omega_n/\omega_s\right)^2} \, . \tag{6.1.25}$$

If we consider only one eigenmode ω_0 to be of significance,

$$W = -\frac{1}{2} \frac{f_0}{\omega_0} \left(1 + \frac{\omega_0}{\omega_s}\right) \int_0^\infty dk \cdot \frac{k^2 \cdot e^{2kz_0}}{k^2 v^2/\omega_s^2 + \left(1 + \omega_0/\omega_s\right)^2} \, ,$$

$$= -\frac{\langle r^2 \rangle}{3} \left(1 + \frac{\omega_0}{\omega_s}\right) \int_0^\infty dk \cdot \frac{k^2 \cdot e^{2kz_0}}{k^2 v^2/\omega_s^2 + \left(1 + \omega_0/\omega_s\right)^2} \, , \tag{6.1.26}$$

where we have used equation (6.1.6). In the static limit the above expression reduces to,

$$W(z, v=0) = -\frac{\langle r^2 \rangle}{12} \cdot \frac{1}{|z_0|^3} \cdot \frac{1}{\left(1 + \omega_0/\omega_s\right)} \, , \tag{6.1.27}$$

which is the standard result due to Bardeen[89].

The result (6.1.26) now incorporates the internal structure of the dipole, and therefore is a modification of (6.1.6). This result again in a new one. However, as already described in the previous section, there is no significant effect of the velocity dependence.

6.2 ATOM APPROACHING A METAL SURFACE WITH A LAYER OF ADSORBED MOLECULES

In this case we have studied only the energy loss probability . Representing the adsorbed molecule by an oscillating point dipole we study the interaction between a moving atom and such adsorbed molecules within the pure image model. Since the energy of the incident particles is quite low ($\sim$ 0.05 eV) i.e. less than the threshold $\hbar\omega_s$ for excitation of surface plasmons, in this model we approximate the interaction between incoming dipole and plasmons and that between adsorbed molecules and plasmons by the classical image interaction. Using classical image theory in this way amounts to treating the metal substrate as a perfect conductor or neglecting the dynamical nature of the plasmon response[90]. This is justified because of the low energy associated with the incoming particle. The Hamiltonian can then be diagonalised to obtain,

$$H = H_a + V(\underset{\sim}{r}) + \sum_i \hbar\omega_\perp a_i^\dagger a_i + \sum_i E_i(\underset{\sim}{r}) \left(\frac{e_2^2 \hbar}{2m_a\omega_\perp}\right)^{1/2} (a_i + a_i^\dagger) \quad . \qquad (6.2.1)$$

Here, H_a is the unperturbed Hamiltonian for the incoming atom ;

i refers to the site of the adsorbed molecule, $(\hbar e_2^2/2m_a\omega_\perp)^{1/2}$ represents the z-component of the dipole moment of the adsorbed molecule treated as a point dipole oscillator ; $E_i(r)$ is the z-component of the effective electric field at the molecular site i ; and $\omega_\perp$ is the frequency of the adsorbed molecule softened by interaction with its own image[90]. The effective interaction is then between incoming dipole, its image and the adsorbed dipole. Below,we follow essentially the method suggested by Delanaye et al. for an incoming charge[90].

The quantity of interest in the experiments is the so called single loss probability $\bar{P}_{1a}$, namely the ratio of the intensities of the single loss line occurring at $\epsilon_o - h\omega_\perp$ and the no loss line at ϵ_o , where ϵ_o is the incident energy of the particle. $\bar{P}_{1a}$ is given by $e^{-Q}\,Q$ ($\simeq Q$ for small Q) where Q is the average number of excitations excited. Q is given by the ratio of the total energy transferred to the adsorbed molecules and the energy $(\hbar\omega_\perp)$ of the oscillator corresponding to the adsorbed molecule i.e., by[90] ,

$$Q = \sum_i |e_2 E_i(\omega_\perp)|^2 / 2\hbar m_a \omega_\perp \,. \qquad (6.2.2)$$

We have to find the effective field $\underset{\sim}{\xi}(\underset{\sim}{r},\underset{\sim}{r}_i)$ at the molecule site i. The incoming atom is assumed to move at a constant speed $\underset{\sim}{v}$ along the classical trajectory $\underset{\sim}{r} = (\underset{\sim}{v}_{\parallel} t, \underset{\sim}{v}_{\perp} t)$, In this case the effective potential V_i, at site i is,

$$V_i(\omega_\perp) = |e_1 \Delta z| \frac{\partial}{\partial z} \int_{-\infty}^{\infty} dt\, e^{i\omega_\perp t} \left(\frac{1}{|\underset{\sim}{r} - \underset{\sim}{r}_i|} - \frac{1}{|\underset{\sim}{r} - \underset{\sim}{r}_i'|} \right), \qquad (6.2.3)$$

where $|e_1 \Delta z|$ is the strength of the dipole moment of the incoming dipole ; $\underset{\sim}{r}_i$ and $\underset{\sim}{r}'_i$ are the coordinates of the adsorbed molecule and its image respectively so that $\underset{\sim}{r}_i = (\underset{\sim}{\rho}_{oi}, z_o)$ and $\underset{\sim}{r}'_i = (\underset{\sim}{\rho}_{oi}, -z_o)$ where $\underset{\sim}{\rho}_{oi}$ is the relative coordinate between the adsorbed molecule and the impact point of the incoming dipole. Taking the two-dimensional Fourier transform in x-y plane,

$$V_i(\omega_\perp) = \left(\frac{e_1^2 \hbar}{2m_o\omega_o}\right)^{1/2} \cdot \frac{\partial}{\partial z} \int_{-\infty}^{\infty} dt\, e^{i\omega_\perp t} \int \frac{d^2k}{(2\pi)^2}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}_{oi} + i\underset{\sim}{k}\cdot\underset{\sim}{v}_{11} t} \cdot \frac{2\pi}{k}$$

$$\cdot \left[e^{-k|z-z_o|} - e^{-k|z+z_o|}\right],$$

$$= \left(\frac{e_1^2 \hbar}{2m_o\omega_o}\right)^{1/2} \int \frac{d^2k}{(2\pi)^2} \cdot e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}_{oi}} \frac{2\pi}{k} \frac{4k(\omega_\perp + \underset{\sim}{k}\cdot\underset{\sim}{v}_{11})}{(\omega_\perp + \underset{\sim}{k}\cdot\underset{\sim}{v}_{11})^2 + k^2 v_\perp^2} \cdot \sin\left[\frac{(\omega_\perp + \underset{\sim}{k}\cdot\underset{\sim}{v}_{11}) z_o}{v_\perp}\right] \qquad (6.2.4)$$

In the above equation $(e_1^2\, h/2m_o\omega_o)^{1/2}$ is the dipole moment of the incoming dipole. To ensure specular reflection if we assume that the incoming particle is moving along $\underset{\sim}{r} = (0, v|t|)$ we can set $\underset{\sim}{v}_{11} = 0$ in above equation to obtain,

$$V_i(\omega_\perp) = \left(\frac{e_1^2 \hbar}{2m_o\omega_o}\right)^{1/2} \int \frac{d^2k}{(2\pi)^2} \cdot \frac{2\pi}{k}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}_{oi}} \frac{4k\omega_\perp}{\omega_\perp^2 + k^2 v^2} \sin\left(\frac{\omega_\perp z_o}{v}\right) \qquad (6.2.4a)$$

The z component of the effective field at molecular site i is then given by,

$$E_i(\omega_\perp) = \frac{\partial}{\partial z_o} V_i(\omega_\perp),$$

$$= \left(\frac{e_1^2 \hbar}{2m_o\omega_o}\right)^{1/2} \int \frac{d^2k}{2\pi k}\, e^{i\underset{\sim}{k}\cdot\underset{\sim}{\rho}_{oi}} \frac{4k\omega_\perp}{\omega_\perp^2 + k^2 v^2} \left(\frac{\omega_\perp}{v}\right) \cos\left(\frac{\omega_\perp z_o}{v}\right) \qquad (6.2.5)$$

Using this expression for effective field in equation (6.2.2),

we obtain,

$$Q = \frac{e_2^2}{2\hbar m_a \omega_\perp} \cdot \frac{e_1^2 \hbar}{2 m_0 \omega_0} \int \frac{d^2k}{(2\pi)^2} \cdot \frac{2\pi}{k} \frac{4k\omega_\perp}{\omega_\perp^2 + k^2 v^2} \cdot \int \frac{d^2k'}{(2\pi)^2} \cdot \frac{2\pi}{k'} \cdot \frac{4k'.\omega_\perp}{\omega_\perp^2 + k'^2 v^2}$$
$$\left(\frac{\omega_\perp}{v}\right)^2 \cos^2\left(\frac{\omega_\perp z_0}{v}\right) \sum_i e^{i(\underset{\sim}{k} - \underset{\sim}{k}').\underset{\sim}{s}_{0i}} .$$

Assuming that the adsorbed molecules form an uniform periodic layer with square unit cells of area a^2 each, we can average over them to get,

$$\sum_i e^{i(\underset{\sim}{k} - \underset{\sim}{k}').\underset{\sim}{s}_{0i}} = \frac{(2\pi)^2}{a^2} \sum_{\underset{\sim}{g}} e^{i\underset{\sim}{g}.\underset{\sim}{s}_0} \delta(\underset{\sim}{k} - \underset{\sim}{k}' - \underset{\sim}{g}) , \qquad (6.2.6)$$

where $\underset{\sim}{s}_0$ is the impact point of the atom on the surface. The expression for Q, thus still depends on the impact point. We average out this dependence by integration over all possible $\underset{\sim}{s}_0$ which yields $(2\pi/a)^2 \delta(\underset{\sim}{k} - \underset{\sim}{k}')$ in place of (6.2.6). Using this and expressing the induced dipole moment[88] in terms of its static polarisability α, we obtain

$$Q = \frac{8\pi}{a^2} \alpha_a \omega_\perp \alpha_0 \omega_0 \cos^2\left(\frac{\omega_\perp z_0}{v}\right) \frac{\omega_\perp^2}{v^4} \int_0^{y_c} dy \frac{y}{(1+y^2)^2} , \qquad (6.2.7)$$

where, $y = kv/\omega_\perp$. The upper limit on the k-integral is necessary to take into account one or both of the following physical constraints[90]. (i) The momentum transfer to the molecule is bounded by the fact that the adsorbed molecular dipole has a finite size instead of being a point dipole as assumed by the model. (ii) The maximum momentum transfer is also dependent on the spectrometer aperture θ_c which excludes all particles which have exicted surface vibrations of momentum larger than $k_c = k_0 \theta_c$ where k_0 is the incident momentum. Typical apertures used in experiments are of the order of 0.1 radians[90]. This gives,

$$y_c = \frac{k_c v}{\omega_\perp} = \left(\frac{2E_0}{\hbar\omega_\perp}\right)\theta_c \,. \qquad (6.2.8)$$

Evaluation of y-integral yields,

$$Q = \frac{4\pi}{a^2}\,\frac{\alpha_a\omega_\perp\,\alpha_0\omega_0}{v^4}\,\omega_\perp^2\cos^2\left(\frac{\omega_\perp z_0}{v}\right)\,\frac{y_c^2}{1+y_c^2}\,. \qquad (6.2.9)$$

We evaluated Q numerically for atoms approaching a metal surface with carbon monoxide molecules adsorbed over it. We choose the following parameters for the adsorbate[90] : $z_0 = 1.5\ A^0$, $\hbar\omega_\perp = 0.25$ eV, $a = 3A^0$ and $\alpha_a = 2A^{0\,3}$ [91]. Assuming that the incident particle was a Neon atom with incident energy 0.05 eV ($\alpha_0 = 0.39\ A^{0\,3}$ and $\hbar\omega_0 = 16.67$ eV[91]), we find that even for very small θ_c (of the order of 0.15^0), the Q values obtained are very large giving $\bar{P}_{1a}$ nearly equal to zero. A look at equation (6.2.9) suggests that for lower w values, the Q values would reduce drastically to give non-zero $\bar{P}_{1a}$. A sample calculation taking $\hbar\omega$ = 0.1 eV and keeping the same values for all other constants gives non-zero values of $\bar{P}_{1a}$ for very small values of spectrometer aperture. Table (6.1) shows the values for Q and $\bar{P}_{1a}$ in these calculations.

Table 6.1

θ_c(in deg.)	Q	$\bar{P}_{1a}$
0.15	0.2665	0.2042
0.45	2.3986	0.2179
0.85	8.5568	0.0016
1.00	11.8423	0 (10^{-5})

6.3 DISCUSSION

We have derived here the formulae for dynamic van der Waals interaction which forms the attractive part of the interaction between a moving atom and a plane metal surface. We obtain expressions for $W(z,v)$ using the model Hamiltonian approach as well as the dielectric response approach, but find that due to the large mass of the atom, the velocity of the particle is too small to have any effect on the vdW interaction, thus giving no improvement over the static results for any distances of significance. Using a pure image model we also calculate single loss probability $\bar{P}_{1a}$ for an atom approaching a metal surface with an uniform layer (coverage less than one) of adsorbed molecules. Though in the example chosen, i.e for a layer of CO molecules $\bar{P}_{1a}$ is seen to be very small, it is noted that for lower frequencies of excitation for the adsorbed molecules it is possible to get a non-zero $\bar{P}_{1a}$. This means that it should be possible to detect changes in adsorbed molecule (for example the change in vibrational frequency of a molecule) due to its adsorption on a metallic surface from an atomic or molecular scattering experiment.

APPENDIX I

We define the following retarded and time ordered correlation functions

$$\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t) = \frac{\theta(t)}{i\hbar V}\left\langle\left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t),\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},0)\right]_{-}\right\rangle_{eq}; \qquad (A\cdot1\cdot1)$$

and

$$\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t) = \frac{\theta(t)}{i\hbar V}\left\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},0)\right\rangle_{eq} + \frac{\theta(-t)}{i\hbar V}\left\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},-t)\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},0)\right\rangle_{eq}, \qquad (A\cdot1\cdot2)$$

where,

$$\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) - \langle\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\rangle_{eq}, \qquad (A\cdot1\cdot3)$$

and

$$\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\,\sigma}(t)\,a_{\underset{\sim}{k}+\underset{\sim}{q}/2\,\sigma}(t).$$

At T = 0, we can write,

$$\left\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},0)\right\rangle_{eq} = \sum_{n}\langle 0|\,e^{iHt/\hbar}\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,e^{-iHt/\hbar}|n\rangle\langle n|\,\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})|0\rangle,$$

where we have introduced a complete set of wave vectors $\{|n\rangle\}$ i.e. states of the interacting system where $|0\rangle$ is the ground state and $H|n\rangle = \omega_n|n\rangle$. Writing $\omega_{no} = \omega_n - \omega_o$.

$$\langle 0|\,e^{iHt/\hbar}\,\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,e^{-iHt/\hbar}|n\rangle = \langle 0|\,\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})|n\rangle\,e^{-i\omega_{no}t} = M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,e^{-i\omega_{no}t}. \qquad (A\cdot1\cdot4)$$

Then,

$$\left[\langle n|\,\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})|0\rangle\right]^{*} = \langle 0|\,\hat{\tilde{\rho}}^{+}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})|n\rangle = \langle 0|\,\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})|n\rangle = M^{on}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}).$$

so that,

$$\langle n|\,\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})|0\rangle = M^{on\,*}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}) \qquad (A\cdot1\cdot5)$$

Expressing the matrix elements in terms of these $M^{on}_{\underset{\sim}{k}\sigma}$ etc.,

we have,

$$\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\,\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},0)\rangle_{eq} = \sum_n M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on\,*}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\,e^{-i\omega_{no}t}. \qquad (A\cdot1\cdot6)$$

Similarly,

$$\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},0)\,\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)\rangle_{eq} = \sum_n M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on\,*}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})\,e^{i\omega_{no}t}. \qquad (A\cdot1\cdot7)$$

Substituting these results in the expression for $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},t)$ and taking its temporal Fourier transform we have,

$$\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \frac{1}{\hbar V}\sum_n\left[\frac{M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on\,*}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})}{\omega+i\delta-\omega_{no}} - \frac{M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on\,*}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})}{\omega+i\delta+\omega_{no}}\right]. \qquad (A\cdot1\cdot8)$$

$M^{on}_{k\sigma}$ etc., are taken to be real quantities.

The real and imaginary parts of $\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ are then given by,

$$\mathrm{Re}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \frac{1}{\hbar V}\sum_n\left[P\,\frac{M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})}{\omega-\omega_{no}} - P\,\frac{M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})}{\omega+\omega_{no}}\right] \qquad (A\cdot1\cdot9a)$$

and

$$\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = -\frac{\pi}{\hbar V}\sum_n\Big[M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\,\delta(\omega-\omega_{no}) - M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})\,\delta(\omega+\omega_{no})\Big]. \qquad (A\cdot1\cdot9b)$$

Utilising the fact that the matrix elements $M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})$ etc., are real, it can be easily shown that,

$$\mathrm{Re}\,\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},-\omega) = \mathrm{Re}\,\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega), \qquad (A\cdot1\cdot10a)$$

and

$$\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},-\omega) = -\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega). \qquad (A\cdot1\cdot10b)$$

From these two relations it also follows that,

$$[\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)]^* = \chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},-\omega). \qquad (A\cdot1\cdot11)$$

Further,

$$\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},\omega) = \chi^r_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega). \qquad (A\cdot1\cdot12)$$

which leads to the result,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) = f^{(2)eq}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}). \qquad (A\cdot1\cdot13)$$

Most workers (e.g., Niklasson[9], Sharma et al.[12]) have assumed that,

$$f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}) = f^{(2)eq}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}).$$

This assumption is incorrect as is shown by the previous expression. This result also follows directly from the definition of $f^{(2)eq}$ and the density operators $\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$. We can write similar expressions for the causal function defined in (A.1.2). In this case we have,

$$\chi^c_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \frac{1}{\hbar V}\sum_n\left[\frac{M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})}{\omega+i\delta-\omega_{no}} - \frac{M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})}{\omega-i\delta+\omega_{no}}\right], \qquad (A\cdot1\cdot14)$$

where again we have assumed that $M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})$ etc., are real quantities. It then follows that,

$$\mathrm{Re}\;\chi^c_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \mathrm{Re}\;\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega), \qquad (A\cdot1\cdot15a)$$

and

$$\mathrm{Im}\;\chi^c_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \mathrm{sgn}(\omega)\,\mathrm{Im}\;\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega). \qquad (A\cdot1\cdot15b)$$

An important result follows from equation (A.1.6),

$$\langle\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\rangle_{eq} = \sum_n M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q}),$$

$$= \int_0^\infty d\omega \sum_n M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\, M^{on}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\, \delta(\omega-\omega_{no}),$$

$$= -\frac{\hbar V}{\pi}\int_0^\infty d\omega\ \mathrm{Im}\,\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\ . \qquad (A.1.16)$$

Here we have used the fact that by definition itself $\omega_{no}>0$, in the second line and the expression (A.1.9b) for $\mathrm{Im}\,\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ in the third line. Similarly we can show starting with the expression for $\chi^c_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ (equation A.1.14), that

$$\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\rangle_{eq} = -\frac{\hbar V}{\pi}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\chi^c_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\,, \qquad (A.1.17)$$

where in the contour integration we close the contour in the lower half plane.

Lehmann representations

$$\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = \int_{-\infty}^{\infty}d\omega'\cdot\frac{1}{\hbar V}\sum_n\left[\frac{M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q})\,\delta(\omega'-\omega_{no})}{\omega+i\delta-\omega'}\right.$$

$$\left. - \frac{M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})\,\delta(\omega'+\omega_{no})}{\omega+i\delta+\omega'}\right],$$

$$= \int_{-\infty}^{\infty}\frac{d\omega'}{\omega+i\delta-\omega'}\ \frac{1}{\hbar V}\sum_n\left[M^{on}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})M^{on}_{\underset{\sim}{k}'\sigma'}(+\underset{\sim}{q})\,\delta(\omega'-\omega_{no})\right.$$

$$\left. - M^{on}_{\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q})\,M^{on}_{\underset{\sim}{k}\sigma}(-\underset{\sim}{q})\,\delta(\omega'+\omega_{no})\right],$$

$$= -\frac{1}{\pi}\int_{-\infty}^{\infty}d\omega'\ \frac{\mathrm{Im}\,\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')}{\omega+i\delta-\omega'} \qquad (A.1.18)$$

Here, in the second line we have changed the sign of ω' in the second term and used the expression (A.1.9b) for $\mathrm{Im}\,\chi^r_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)$ in the third line. Similarly we have,

$$\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = -\frac{1}{\pi}\int_{-\infty}^{\infty} d\omega'\ \mathrm{Im}\,\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')\left[\frac{\Theta(\omega')}{\omega+i\delta-\omega'} - \frac{\Theta(-\omega')}{\omega-i\delta-\omega'}\right], \tag{A.1.19a}$$

$$= -\frac{1}{\pi}\int_{-\infty}^{\infty} d\omega'\ \mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')\left[\frac{\Theta(\omega')}{\omega+i\delta-\omega'} + \frac{\Theta(-\omega')}{\omega-i\delta-\omega'}\right]. \tag{A.1.19b}$$

In writing in terms of the retarded function, we have used the relation between the imaginary parts of the retarded and the causal function (equation (A.1.15b)). Some more symmetry relations can be written down using equations (A.1.11), (A.1.10) and (A.1.15). These are,

$$\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega) = -\mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},\omega) = -\mathrm{Im}\,\chi^{r}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega); \tag{A.1.20a}$$

and

$$\mathrm{Re}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega) = \mathrm{Re}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},\omega) = \mathrm{Re}\,\chi^{r}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega). \tag{A.1.20b}$$

In contrast, when the variables $\underset{\sim}{k}\sigma$ and $\underset{\sim}{k}'\sigma'$ are summed over, we have,

$$\mathrm{Im}\,\chi^{r}(\underset{\sim}{q},-\omega) = -\mathrm{Im}\,\chi^{r}(\underset{\sim}{q},\omega)\ ; \tag{A.1.21a}$$

and

$$\mathrm{Re}\,\chi^{r}(\underset{\sim}{q},-\omega) = \mathrm{Re}\,\chi^{r}(\underset{\sim}{q},\omega)\ . \tag{A.1.21b}$$

Similarly, we have for the causal functions,

$$\mathrm{Re}\,\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega) = \mathrm{Re}\,\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},\omega) = \mathrm{Re}\,\chi^{c}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega); \tag{A.1.22a}$$

and

$$\mathrm{Im}\,\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega) = \mathrm{Im}\,\chi^{c}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},\omega) = \mathrm{Im}\,\chi^{c}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega), \tag{A.1.22b}$$

$$= -\,\mathrm{sgn}\,\omega\ \mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega) = \mathrm{sgn}\,\omega\ \mathrm{Im}\,\chi^{r}_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(-\underset{\sim}{q},\omega)$$

$$= \mathrm{sgn}\,\omega\ \mathrm{Im}\,\chi^{r}_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega)\ . \tag{A.1.22c}$$

Then we obtain for the causal response function $\chi^c(\underset{\sim}{q},\omega)$,

$$\text{Re}\,\chi^c(\underset{\sim}{q},-\omega) = \text{Re}\,\chi^c(\underset{\sim}{q},\omega) = \text{Re}\,\chi^r(\underset{\sim}{q},\omega) \qquad (A\cdot1\cdot23a)$$

and

$$\text{Im}\,\chi^c(\underset{\sim}{q},-\omega) = \text{Im}\,\chi^c(\underset{\sim}{q},\omega) = \text{sgn}\,\omega\ \text{Im}\,\chi^r(\underset{\sim}{q},\omega) \qquad (A\cdot1\cdot23b)$$

We use these relations given in equations (A.1.20) and (A.1.22) to obtain the Lehmann representations for $\chi^x(\underset{\sim}{q},\omega)$ and $\chi^r(\underset{\sim}{q},\omega)$. From equation (A.1.19b), we have,

$$\chi^c_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = -\frac{1}{\pi}\int_0^\infty d\omega'\left[\frac{\text{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')}{\omega+i\delta-\omega'} - \frac{\text{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega')}{\omega-i\delta+\omega'}\right],$$

$$= -\frac{1}{\pi}\int_0^\infty d\omega'\left[\frac{\text{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')}{\omega+i\delta-\omega'} - \frac{\text{Im}\,\chi^r_{-\underset{\sim}{k}\sigma\,-\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')}{\omega-i\delta+\omega'}\right].$$

Summing over the indices $\underset{\sim}{k}\sigma$ and $\underset{\sim}{k}'\sigma'$ yields,

$$\chi^c(\underset{\sim}{q},\omega) = -\frac{1}{\pi}\int_0^\infty d\omega'\ \text{Im}\,\chi^r(\underset{\sim}{q},\omega')\left\{\frac{1}{\omega+i\delta-\omega'} - \frac{1}{\omega-i\delta+\omega'}\right\}. \qquad (A\cdot1\cdot24)$$

which is the well-known usual result. Similarly on starting with the expression (A.1.18), we have,

$$\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega) = -\frac{1}{\pi}\int_{-\infty}^\infty d\omega'\ \frac{\text{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')}{\omega+i\delta-\omega'},$$

$$= -\frac{1}{\pi}\int_0^\infty d\omega'\left[\frac{\text{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},\omega')}{\omega+i\delta-\omega'} + \frac{\text{Im}\,\chi^r_{\underset{\sim}{k}\sigma\,\underset{\sim}{k}'\sigma'}(\underset{\sim}{q},-\omega')}{\omega+i\delta+\omega'}\right]. \qquad (A\cdot1\cdot25)$$

Summing over the variables $\underset{\sim}{k}\sigma$ and $\underset{\sim}{k}'\sigma'$, we have

$$\chi^r(\underset{\sim}{q},\omega) = -\frac{1}{\pi}\int_0^\infty d\omega'\left[\frac{\text{Im}\,\chi^r(\underset{\sim}{q},\omega')}{\omega+i\delta-\omega'} + \frac{\text{Im}\,\chi^r(\underset{\sim}{q},-\omega')}{\omega+i\delta+\omega'}\right],$$

$$= -\frac{1}{\pi}\int_0^\infty d\omega' \; \mathrm{Im}\,\chi^r(\underset{\sim}{q},\omega')\left[\frac{1}{\omega+i\delta-\omega'} - \frac{1}{\omega+i\delta+\omega'}\right],$$

$$= \frac{\mu}{\pi}\int_0^\infty d\omega' \; S(\underset{\sim}{q},\omega')\left[\frac{1}{\omega+i\delta-\omega'} - \frac{1}{\omega+i\delta+\omega}\right], \qquad (A\cdot 1\cdot 26)$$

which is a standard result and where we have used the relation

$$S(\underset{\sim}{q},\omega) = -\frac{\mu}{\pi}\,\mathrm{Im}\,\chi^r(\underset{\sim}{q},\omega)\,, \qquad (A\cdot 1\cdot 27)$$

between retarded density-density response function $\chi^r(\underset{\sim}{q},\omega)$ and the dynamic structure factor $S(\underset{\sim}{q},\omega)$ of the system.

APPENDIX II

The Hamiltonian for an electron gas in the presence of an external potential $\phi_{ext}(\underset{\sim}{r},t)$, can be written as,

$$H(t) = \sum_{\sigma} \int d^3r \; \hat{\psi}^{+}_{\sigma}(\underset{\sim}{r},t) \left(-\frac{\hbar^2\nabla^2}{2m}\right) \hat{\psi}_{\sigma}(\underset{\sim}{r},t)$$

$$+ \sum_{\sigma} \int d^3r \; \hat{\psi}^{+}_{\sigma}(\underset{\sim}{r},t) \; \phi_{ext}(\underset{\sim}{r},t) \hat{\psi}_{\sigma}(\underset{\sim}{r},t)$$

$$+ \frac{1}{2} \sum_{\sigma\sigma'} \int d^3r \, d^3r' \; \hat{\psi}^{+}_{\sigma}(\underset{\sim}{r},t) \hat{\psi}^{+}_{\sigma'}(\underset{\sim}{r}',t) \, v(\underset{\sim}{r}-\underset{\sim}{r}') \hat{\psi}_{\sigma'}(\underset{\sim}{r}',t) \hat{\psi}_{\sigma}(\underset{\sim}{r},t),$$

where $v(\underset{\sim}{r}-\underset{\sim}{r}')$ is the Coulomb potential. $\hat{\psi}_{\sigma}(\underset{\sim}{r},t)$ is the field operator which can be expanded in terms of the creation and destruction operators $a^{+}_{\underset{\sim}{k}\sigma}(t)$ and $a_{\underset{\sim}{k}\sigma}(t)$ as ,

$$\hat{\psi}_{\sigma}(\underset{\sim}{r},t) = \frac{1}{\sqrt{V}} \sum_{\underset{\sim}{k}} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \, a_{\underset{\sim}{k}\sigma}(t) \; ;$$

and

$$\hat{\psi}^{+}_{\sigma}(\underset{\sim}{r},t) = \frac{1}{\sqrt{V}} \sum_{\underset{\sim}{k}} e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}} \, a^{+}_{\underset{\sim}{k}\sigma}(t).$$

In terms of these operators then,

$$H(t) = \sum_{\underset{\sim}{k}\sigma} \frac{\hbar^2k^2}{2m} \, a^{+}_{\underset{\sim}{k}\sigma}(t) \, a_{\underset{\sim}{k}\sigma}(t) + \frac{1}{V} \sum_{\underset{\sim}{q}} \phi_{ext}(-\underset{\sim}{q},t) \sum_{\underset{\sim}{k}\sigma_1} a^{+}_{\underset{\sim}{k},\sigma_1}(t) a_{\underset{\sim}{k},\sigma_1}(t)$$

$$+ \frac{1}{2V} \sum_{\underset{\sim}{q}} v(\underset{\sim}{q}) \sum_{\sigma\sigma'} \sum_{\underset{\sim}{k}_1\underset{\sim}{k}_2} a^{+}_{\underset{\sim}{k}_1\sigma}(t) \, a^{+}_{\underset{\sim}{k}_2\sigma'}(t) \, a_{\underset{\sim}{k}_2-\underset{\sim}{q}\sigma'}(t) \, a_{\underset{\sim}{k}_1+\underset{\sim}{q}\sigma}(t),$$

where $v(q)$ and $\phi_{ext}(q,t)$ are the space Fourier transforms of $v(\underset{\sim}{r},t)$ and $\phi_{ext}(\underset{\sim}{r},t)$ respectively. On further simplification, we get,

$$H(t) = \sum_{\underset{\sim}{k}\sigma} \frac{\hbar^2k^2}{2m} \, a^{+}_{\underset{\sim}{k}\sigma}(t) \, a_{\underset{\sim}{k}\sigma}(t) + \frac{1}{V} \sum_{\underset{\sim}{q}} \phi_{ext}(-\underset{\sim}{q},t) \sum_{\underset{\sim}{k}\sigma} a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t) \, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t)$$

$$+ \frac{1}{2V} \sum_{\underset{\sim}{q}} v(\underset{\sim}{q}) \sum_{\substack{\underset{\sim}{k}\sigma \\ \underset{\sim}{k}'\sigma'}} a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t) \, a^{+}_{\underset{\sim}{k}'+\underset{\sim}{q}/2\sigma'}(t) \, a_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}(t) \, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t). \qquad (A.2.1)$$

The Coulomb potential in Fourier space is given by,

$$v(q) = \frac{4\pi e^2}{q^2} \quad , \quad \text{for } q \neq 0$$
$$= 0 \quad , \quad \text{for } q = 0 .$$

This is because the potential part includes the interaction of the electron with the uniform positive background so that on averaging over space, the electron-electron interaction exactly cancels the interaction with the positive background.

An alternative description of H(t) can be given in terms of the density operators. We have,

$$\hat{\rho}(\underset{\sim}{r}, t) = \sum_{\sigma} \psi_{\sigma}^{\dagger}(\underset{\sim}{r}, t)\, \psi_{\sigma}(\underset{\sim}{r}, t)$$
$$= \frac{1}{V} \sum_{\underset{\sim}{q}} e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}} \sum_{\underset{\sim}{k}\sigma} a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t) ,$$
$$= \frac{1}{V} \sum_{\underset{\sim}{q}} e^{i\underset{\sim}{q}\cdot\underset{\sim}{r}}\, \hat{\rho}(\underset{\sim}{q}, t) .$$

Clearly,

$$\hat{\rho}^{\dagger}(\underset{\sim}{q}, t) = \sum_{\underset{\sim}{k}\sigma} a^{\dagger}_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t) = \hat{\rho}(-\underset{\sim}{q}, t) .$$

In terms of these operators we can then write,

$$\sum_{\underset{\sim}{q}} v(\underset{\sim}{q}) \sum_{\substack{\underset{\sim}{k}\sigma \\ \underset{\sim}{k}'\sigma'}} a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a^{\dagger}_{\underset{\sim}{k}'+\underset{\sim}{q}/2\sigma'}(t)\, a_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t)$$

$$= \sum_{\underset{\sim}{q}} v(\underset{\sim}{q}) \sum_{\underset{\sim}{k}\sigma} a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t)\, a^{\dagger}_{\underset{\sim}{k}'+\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}(t)$$
$$- \sum_{\underset{\sim}{q}} v(\underset{\sim}{q})\, a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t) .$$

Here,

$$\sum_{\underset{\sim}{k}\sigma} a^{\dagger}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t) = \sum_{\underset{\sim}{k}\sigma} a^{\dagger}_{\underset{\sim}{k}\sigma}(t)\, a_{\underset{\sim}{k}\sigma}(t) = \hat{\rho}(q=0, t) = N .$$

Then we have,

$$H(t) = \sum_{\underset{\sim}{k}\sigma} \frac{\hbar^2 k^2}{2m}\, a^{\dagger}_{\underset{\sim}{k}\sigma}(t)\, a_{\underset{\sim}{k}\sigma}(t) + \frac{1}{V} \sum_{\underset{\sim}{q}} \phi_{ext}(-\underset{\sim}{q}, t)\, \hat{\rho}(\underset{\sim}{q}, t)$$
$$+ \frac{1}{2V} \sum_{\underset{\sim}{q}} v(\underset{\sim}{q}) \left[\hat{\rho}(\underset{\sim}{q}, t)\, \hat{\rho}(-\underset{\sim}{q}, t) - N \right] . \qquad (A \cdot 2 \cdot 2)$$

APPENDIX III

We want to evaluate the integral,

$$\int_{-\infty}^{\infty} \frac{d\omega'}{2\pi i}\, \chi^c(q_1, \omega')\, \chi^c(q_2, \omega - \omega')$$

$$= \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi i} \left(-\frac{1}{\pi}\right) \int_0^{\infty} d\omega_1\, \mathrm{Im}\, \chi^r(q_1, \omega_1) \left[\frac{1}{\omega' + i\delta_1 - \omega_1} - \frac{1}{\omega' - i\delta_1 + \omega_1}\right]$$

$$\cdot \left(-\frac{1}{\pi}\right) \int_0^{\infty} d\omega_2\, \mathrm{Im}\, \chi^r(q_2, \omega_2) \left[\frac{1}{\omega - \omega' + i\delta_2 - \omega_2} - \frac{1}{\omega - \omega' - i\delta_2 + \omega_2}\right],$$

$$= \frac{1}{\pi^2} \int_0^{\infty} d\omega_1\, \chi^{r''}(q_1, \omega_1) \int_0^{\infty} d\omega_2\, \chi^{r''}(q_2, \omega_2)$$

$$\cdot \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi i} \left[\frac{1}{\omega' + i\delta_1 - \omega_1} - \frac{1}{\omega' - i\delta_1 + \omega_1}\right] \left[\frac{1}{\omega - \omega' + i\delta_2 - \omega_2} - \frac{1}{\omega - \omega' - i\delta_2 + \omega_2}\right].$$

Closing the contour for ω' integration, in the upper half plane, we have,

$$= \frac{1}{\pi^2} \int_0^{\infty} d\omega_1\, \chi^{r''}(q_1, \omega_1) \int_0^{\infty} d\omega_2\, \chi^{r''}(q_2, \omega_2) \left[-\frac{1}{-\omega_1 - \omega - \omega_2 + i\delta_1 + i\delta_2}\right.$$

$$\left. + \frac{1}{-\omega_1 - \omega + \omega_2 + i\delta_1 - i\delta_2} - \frac{1}{\omega - \omega_2 - \omega_1 + i\delta_1 + i\delta_2} + \frac{1}{\omega + \omega_1 - \omega_2 - i\delta_1 + i\delta_2}\right],$$

$$= \frac{1}{\pi^2} \int_0^{\infty} d\omega_1 \chi^{r''}(q_1, \omega_1) \int_0^{\infty} d\omega_2\, \chi^{r''}(q_2, \omega_2) \left[\frac{1}{\omega + \omega_1 + \omega_2 + i\delta} - \frac{1}{\omega - \omega_1 - \omega_2 + i\delta}\right] \cdot \quad (A.3.1)$$

We have denoted the infinitesimal imaginary parts by δ_1 and δ_2 in the spectral representation of the different causal functions. This is an important detail for any such contour integration and so we have given the explicit steps involved. Using (A.3.1), we can write,

$$\mathrm{Im} \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi i}\, \chi^c(q', \omega')\, \chi^c(q'', \omega - \omega')$$

$$= -\frac{\pi}{\pi^2} \int_0^{\infty} d\omega_1\, \chi^{r''}(q', \omega_1) \int_0^{\infty} d\omega_2\, \chi^{r''}(q'', \omega_2) \left[\delta(\omega + \omega_1 + \omega_2) - \delta(\omega - \omega_1 - \omega_2)\right],$$

$$= \frac{1}{\pi}\int_0^\infty d\omega_1\, \chi''(\underset{\sim}{q}',\omega_1)\ \chi''(\underset{\sim}{q}'',\omega-\omega_1)\,\theta(\omega-\omega_1) \quad , \text{for } \omega>0,$$

$$= \frac{1}{\pi}\int_0^\omega d\omega_1\, \chi''(\underset{\sim}{q}',\omega_1)\,\chi''(\underset{\sim}{q}'',\omega-\omega_1)\,. \qquad (A.3.2)$$

Similarly using the same method as used for (A.3.1) we obtain

$$\left(-\frac{1}{\pi}\right)\int_0^\infty d\omega_2 \int_{-\infty}^{\infty}\frac{d\omega'}{2\pi i}\, e^{i\omega'\epsilon}\left[\frac{1}{\omega'+\omega-\omega_1+i\delta_1}-\frac{1}{\omega'+\omega+\omega_1-i\delta_1}\right]$$

$$\cdot\left[\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(-\underset{\sim}{q}',\omega_2)}{\omega'-\omega_2+i\delta_2}-\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)}{\omega'+\omega_2-i\delta_2}\right]$$

$$= \left(-\frac{1}{\pi}\right)\int_0^\infty d\omega_2\left[-\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(-\underset{\sim}{q}',\omega_2)}{-\omega-\omega_1-\omega_2+i\delta_1+i\delta_2}-\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)\cdot\right.$$

$$\left.\left\{\frac{1}{-\omega_2+\omega-\omega_1+i\delta_1+i\delta_2}-\frac{1}{-\omega_2+\omega+\omega_1-i\delta_1+i\delta_2}-\frac{1}{-\omega-\omega_1+\omega_2+i\delta_1-i\delta_2}\right\}\right],$$

$$= \left(-\frac{1}{\pi}\right)\int_0^\infty d\omega_2\left[\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(-\underset{\sim}{q}',\omega_2)}{\omega+\omega_1+\omega_2-i\delta}-\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)}{\omega-\omega_1-\omega_2+i\delta}\right],$$

$$= \left(-\frac{1}{\pi}\right)\int_0^\infty d\omega_2\left[-\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)}{\omega+\omega_1+i\delta+\omega_2}+\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(-\underset{\sim}{q}',\omega_2)}{\omega+\omega_1-i\delta+\omega_2}\right.$$

$$\left.+\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)\left\{\frac{1}{\omega+\omega_1-\omega_2+i\delta_1}-\frac{1}{\omega-\omega_1+i\delta_1-\omega_2}\right\}\right],$$

$$= -\chi^c_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega+\omega_1)-\frac{1}{\pi}\int_0^\infty d\omega_2\left\{\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)}{\omega+\omega_1-\omega_2+i\delta}-\frac{\operatorname{Im}\chi^r_{\underset{\sim}{\kappa}\sigma\underset{\sim}{\kappa}'\sigma'}(\underset{\sim}{q}',\omega_2)}{\omega-\omega_1-\omega_2+i\delta}\right\}.$$

(A.3.3)

APPENDIX IV

We have used the method suggested by Dubois[61] to evaluate integrals of the following kind which appear in the theory of a degenerate electron gas :

$$I(\underset{\sim}{q}) \equiv \int_{\substack{p<1 \\ |\underset{\sim}{p}+\underset{\sim}{q}|>1}} d^3p\, f(\underset{\sim}{p}, \underset{\sim}{q}) \,. \qquad (A.4.1)$$

Here the integration is over all momenta within the Fermi sphere (defined by p = 1), which can be excited outside the sphere by a momentum $\underset{\sim}{q}$. If we introduce a parameter α (all integrals which arise are finite if $\alpha \leq 1$) and define,

$$J(\underset{\sim}{q}, \alpha) = \int_{\substack{p<1 \\ |\underset{\sim}{p}+\alpha\underset{\sim}{q}|>1}} d^3p\, f(\underset{\sim}{p}, \underset{\sim}{q})$$

then,

$$\frac{dJ(\underset{\sim}{q}, \alpha)}{d\alpha} = \int_{p<1} d^3p\, \underset{\sim}{q}\cdot(\underset{\sim}{p}+\alpha\underset{\sim}{q})\,\delta(|\underset{\sim}{p}+\alpha\underset{\sim}{q}|-1)\, f(\underset{\sim}{p}, \underset{\sim}{q}).$$

Changing the variable to $\underset{\sim}{n} = \underset{\sim}{p} + \alpha\,\underset{\sim}{q}$, where $\underset{\sim}{n}$ is a unit vector because of the δ-function present in the integrand, and integrating over α, we have,

$$I(q) = J(q, 1) = \int_0^1 d\alpha \int d\Omega_n\, \underset{\sim}{q}\cdot\underset{\sim}{n}\, f(\underset{\sim}{n}-\alpha\underset{\sim}{q}, \underset{\sim}{q})\,\Theta\left(\underset{\sim}{q}\cdot\underset{\sim}{n} - \frac{\alpha q^2}{2}\right) \text{ if } q \leq 2,$$

$$= q\int_0^{2\pi} d\varphi \int_0^1 d\alpha \int_{q\alpha/2}^1 dx\; x\, f(\underset{\sim}{n}-\alpha\underset{\sim}{q}, \underset{\sim}{q}) \,, \qquad (A.4.2)$$

where $x = \underset{\sim}{q}.\underset{\sim}{n}$ and φ is the polar angle measured about $\underset{\sim}{q}$. Thus, here the limits on the integration are simply incorporated in the integrations over the solid angle. For q > 2, the

restriction $|p+q| > 1$ is automatically satisfied and

$$I(\underset{\sim}{q}) = \int_{p<1} d^3p \, f(\underset{\sim}{p}, \underset{\sim}{q}) \quad , \; q \geq 2 \; . \qquad (A.4.3)$$

We have expressed the integrals of the type (A.4.1) appearing in our calculations by equations of the type (A.4.2) and (A.4.3) and then evaluated the simplified integrals.

APPENDIX V

$$\text{(i)}\ \sum_{\tilde{k}\sigma} \operatorname{Im} F^{(1)}_{\tilde{k}\sigma}(\tilde{q},\tilde{q}',-\omega) = v(\tilde{q}-\tilde{q}')\frac{\lambda}{4\pi}\sum_{\tilde{k}\sigma}\operatorname{Im}\int_0^\infty d\omega_1$$

$$\cdot\left[\frac{\chi^{co}_{\tilde{k}\sigma}(\tilde{q}',\omega_1-\omega)}{\epsilon^c(\tilde{q}',\omega_1-\omega)}\,\chi''(\tilde{q}-\tilde{q}',\omega_1)+\chi^r(\tilde{q}-\tilde{q}',\omega-\omega_1)\operatorname{Im}\left(\frac{\chi^{oo}_{\tilde{k}\sigma}(\tilde{q}',\omega_1)}{\epsilon^r(\tilde{q}',\omega_1)}\right)\right],$$

$$= v(\tilde{q}-\tilde{q}')\frac{\lambda}{4\pi}\sum_{\tilde{k}\sigma}\int_0^\infty d\omega_1\left[\chi''(\tilde{q}-\tilde{q}',-\omega-\omega_1)\operatorname{Im}\left(\frac{\chi^{oo}_{\tilde{k}\sigma}(\tilde{q}',\omega_1)}{\epsilon^r(\tilde{q}',\omega_1)}\right)\right.$$

$$\left.+\operatorname{Im}\left(\frac{\chi^{co}_{\tilde{k}\sigma}(\tilde{q}',\omega_1-\omega)}{\epsilon^c(\tilde{q}',\omega_1-\omega)}\right)\chi''(\tilde{q}-\tilde{q}',\omega_1)\right],$$

$$= v(\tilde{q}-\tilde{q}')\frac{\lambda}{4\pi}\int_0^\infty d\omega_1\left[-\chi''(\tilde{q}-\tilde{q}',\omega+\omega_1)\chi''(\tilde{q}',\omega_1)+\chi^{c''}(\tilde{q}',\omega_1-\omega)\chi''(\tilde{q}-\tilde{q}',\omega_1)\right],$$

$$= v(\tilde{q}-\tilde{q}')\frac{\lambda}{4\pi}\left\{\int_0^\infty d\omega_1\left[-\chi''(\tilde{q}-\tilde{q}',\omega+\omega_1)\chi''(\tilde{q}',\omega_1)+\chi^{c''}(\tilde{q}',\omega_1)\chi''(\tilde{q}-\tilde{q}',\omega+\omega_1)\right]\right.$$

$$\left.+\int_{-\omega}^{0} d\omega_1\,\chi^{c''}(\tilde{q}',\omega_1)\chi''(\tilde{q}-\tilde{q}',\omega+\omega_1)\right\},$$

$$= v(\tilde{q}-\tilde{q}')\frac{\lambda}{4\pi}\int_0^\omega d\omega_1\,\chi^{c''}(\tilde{q}',\omega_1)\chi''(\tilde{q}-\tilde{q}',\omega-\omega_1),$$

$$= v(\tilde{q}-\tilde{q}')\cdot\frac{\lambda}{4\pi}\int_0^\omega d\omega_1\,\chi''(\tilde{q}',\omega_1)\chi''(\tilde{q}-\tilde{q}',\omega-\omega_1). \qquad (A.5.1)$$

Here we have used the relations (A.1.21) and (A.1.23) (obtained in Appendix I), repeatedly for simplification.

... Contd.

(ii) $\sum_{\vec{\rho}\vec{\kappa}} (\vec{b}\cdot\vec{\kappa})\ \mathrm{Im}\ F^{(1)}_{\vec{\rho}\vec{\kappa}}(\vec{q},\vec{b},-\omega)$

$$= \frac{v}{4\pi}(\vec{b}-\vec{b})_\alpha \int_0^\infty d\omega_1 \mathcal{P}\left[\mathrm{Im}\ \frac{\sum_{\vec{\rho}\vec{\kappa}} \rho_{\vec{\kappa}}\chi^{\rho}_{\vec{\rho}\vec{\kappa}}(\vec{b}\cdot\vec{\kappa})}{\epsilon(\vec{b},\omega_1-\omega)}\ \chi_{\mu\nu}(\vec{b}-\vec{b},\omega_1,\omega-\omega_1) \right.$$

$$\left. - \chi_{\mu\nu}(\vec{b}-\vec{b},\omega+\omega_1,\omega_1)\ \mathrm{Im}\ \frac{\sum_{\vec{\rho}\vec{\kappa}} \rho_{\vec{\kappa}}\chi^{\rho}_{\vec{\rho}\vec{\kappa}}(\vec{b}\cdot\vec{\kappa})}{\epsilon(\vec{b},\omega_1)} \right].$$

$$\sum_{\vec{\rho}\vec{\kappa}} \rho_{\vec{\kappa}}\chi^{\rho}_{\vec{\rho}\vec{\kappa}}(\vec{b}\cdot\vec{\kappa})\ \frac{(\vec{b}\cdot\vec{\kappa})\frac{w}{u} - \omega + i\delta + \omega_1}{\omega_{\vec{b}+\vec{\kappa}} - \omega_{\vec{b}-\vec{\kappa}}} = \sum_{\vec{\rho}\vec{\kappa}} (\vec{b}\cdot\vec{\kappa})\ \rho_{\vec{\kappa}}\chi^{\rho}_{\vec{\rho}\vec{\kappa}}(\vec{b}\cdot\vec{\kappa}) = (\omega_1,\vec{b})$$

Can write, $\vec{b}\cdot\vec{\kappa} = \vec{b}\cdot\vec{\kappa}\left(\frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}}\right)$

$$\Rightarrow \sum_{\vec{\rho}\vec{\kappa}} (\vec{b}\cdot\vec{\kappa})\chi^{\rho}_{\vec{\rho}\vec{\kappa}}(\vec{b}\cdot\vec{\kappa}) = (\omega_1,\vec{b})\left(\frac{v}{w}\right) \sum_{\vec{\rho}\vec{\kappa}} \frac{(\vec{b}\cdot\vec{\kappa})\frac{w}{u} - \omega + i\delta + \omega_1}{\omega_{\vec{b}+\vec{\kappa}} - \omega_{\vec{b}-\vec{\kappa}}} \cdot \left(\frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}}\right) \cdot$$

$$\cdot \left(\frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}}\right) \left[\frac{(\vec{b}\cdot\vec{\kappa})\frac{w}{u} - (\omega+\omega_1) + i\delta}{\omega_{\vec{b}+\vec{\kappa}} - \omega_{\vec{b}-\vec{\kappa}}} \right] \left(\frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}}\right) \cdot$$

$$= \left[\frac{\omega_1}{\omega w} \sum_{\vec{\rho}\vec{\kappa}} \frac{\rho_{\vec{\kappa}}}{\omega_{\vec{b}+\vec{\kappa}} - \omega_{\vec{b}-\vec{\kappa}}} + \left(\omega_{\vec{b}+\vec{\kappa}} - \omega_{\vec{b}-\vec{\kappa}}\right) \frac{\omega_1}{w} \right] =$$

$$\simeq \frac{\omega_1}{\omega w}\ \chi^{\rho}_{o\alpha}(\vec{b},\omega_1)\ \left(\frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}}\right) \cdot$$

Similarly, $\sum_{\vec{\rho}\vec{\kappa}} (\vec{b}\cdot\vec{\kappa})\ \chi^{\rho}_{o\vec{\rho}\vec{\kappa}}(\vec{b},\omega_1) = \frac{\omega_1}{\omega w}\ \chi^{\rho}_{o\rho}(\vec{b},\omega_1)$.

$\therefore$ $\sum_{\vec{\rho}\vec{\kappa}} (\vec{b}\cdot\vec{\kappa})\ \mathrm{Im}\ F^{(1)}_{\vec{\rho}\vec{\kappa}}(\vec{q},\vec{b},-\omega)$

$$= \frac{v}{4\pi}(\vec{b}-\vec{b})_\alpha \frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}} \frac{\omega_1}{\omega w} \int_0^\infty d\omega_1 \mathcal{P}\left[(\omega_1,\vec{b})\chi_{\mu\nu}(\vec{b}-\vec{b},\omega-\omega_1,\omega_1)\chi_{\nu\alpha}(\omega-\omega_1,\vec{b}) \right.$$

$$\left. - \omega_1\chi_{\mu\nu}(\vec{b}-\vec{b},\omega+\omega_1,\omega_1)\chi_{\nu\alpha}(\omega_1,\vec{b}) \right],$$

$$= \frac{v}{4\pi}(\vec{b}-\vec{b})_\alpha \frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}} \frac{\omega_1}{\omega w} \left[\int_0^\infty d\omega_1\ \omega_1\chi_{\mu\nu}(\vec{b}-\vec{b},\omega+\omega_1,\omega_1)\chi_{\nu\alpha}(\omega_1,\vec{b}) \right.$$

$$\left. + \int_0^\infty d\omega_1\ \omega_1\chi_{\mu\nu}(\vec{b}-\vec{b},\omega+\omega_1,\omega_1)\chi_{\nu\alpha}(\vec{b},\omega_1) \right],$$

$$= \frac{v}{4\pi}(\vec{b}-\vec{b})_\alpha \frac{\vec{b}\cdot\vec{b}}{\vec{b}\cdot\vec{b}} \frac{\omega_1}{\omega w} \int_0^\omega d\omega_1\ \omega_1\chi_{\mu\nu}(\vec{b}-\vec{b},\omega-\omega_1,\omega_1)\chi_{\nu\alpha}(\vec{b},\omega_1) .$$

(A.5.2)

188

(iii) $\sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q})^2 \; \Gamma^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}, \underset{\sim}{q}', -\omega)$

To evaluate this we need to evaluate $\sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q})^2 \chi^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}', \omega_1)$.

Choosing z axis along q' and a-y plane containing q, we have,

$$(\underset{\sim}{k}\cdot\underset{\sim}{q})^2 = k_x^2 q_x^2 + k_z^2 q_z^2 \; .$$

Now $\langle k_x^2 \rangle$ = averaged over the ϕ angle = $\langle k^2 \sin^2\theta \cos^2\phi \rangle_\phi = \frac{k^2}{2}\sin^2\theta$

$$\langle k_x^2 q_x^2 + k_z^2 q_z^2 \rangle_\phi = \frac{k^2}{2}(1-\cos^2\theta) q_x^2 + k_z^2 q_z^2$$

$$= \left(\frac{k^2}{2} - \frac{k_z^2}{2}\right) q_x^2 + k_z^2 q_z^2 = \frac{k^2}{2}(q^2 - q_z^2) + k_z^2\left(\frac{3}{2}q_z^2 - \frac{q^2}{2}\right)$$

$$= \frac{k^2}{2}\left(q^2 q'^2 - (\underset{\sim}{q}\cdot\underset{\sim}{q}')^2\right) + \frac{(\underset{\sim}{k}\cdot\underset{\sim}{q}')^2}{q'^4}\left(\frac{3}{2}(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2 - \frac{q^2 q'^2}{2}\right).$$

$$\Rightarrow \sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q})^2 \chi^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}', \omega_1)$$

$$= \sum_{\underset{\sim}{k}\sigma} k^2 \chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}', \omega_1)\left(\frac{q^2 q'^2 - (\underset{\sim}{q}\cdot\underset{\sim}{q}')^2}{2q'^2}\right) + \sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q}')^2 \chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}', \omega_1)\left(\frac{3(\underset{\sim}{q}\cdot\underset{\sim}{q}')^2 - q^2 q'^2}{2q'^4}\right).$$

Note that,

$$\sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q}')^2 \chi^{ro}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}', \omega_1)$$

$$= \frac{1}{\hbar V}\sum_{\underset{\sim}{k}\sigma}\left[\frac{\hbar^2}{m^2}(\underset{\sim}{k}\cdot\underset{\sim}{q}')^2 - (\omega_1+i\delta)^2 + (\omega_1+i\delta)^2\right]\frac{m^2}{\hbar^2}\;\frac{n^0_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma} - n^0_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}}{\omega_1 + i\delta - \frac{\hbar}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q}')},$$

$$= \frac{m^2}{\hbar^2}\cdot\frac{1}{\hbar V}\sum_{\underset{\sim}{k}\sigma}\left[-\left\{\frac{\hbar}{m}(\underset{\sim}{k}\cdot\underset{\sim}{q}') + (\omega_1+i\delta)\right\}\left\{n^0_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma} - n^0_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}\right\}\right.$$

$$\left. + \omega_1^2\cdot\frac{n^0_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma} - n^0_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}}{\omega_1 + i\delta - \frac{\hbar}{m}\underset{\sim}{k}\cdot\underset{\sim}{q}'}\right],$$

$$= -\frac{m}{\hbar}\frac{1}{\hbar V}\sum_{\underset{\sim}{k}\sigma} n^0_{\underset{\sim}{k}\sigma}\left[(\underset{\sim}{k}+\frac{\underset{\sim}{q}'}{2})\cdot\underset{\sim}{q}' - (\underset{\sim}{k}-\frac{\underset{\sim}{q}'}{2})\cdot\underset{\sim}{q}'\right] + \frac{m^2\omega_1^2}{\hbar^2}\chi^{ro}(\underset{\sim}{q}', \omega_1),$$

$$= -\frac{mn}{\hbar^2}\cdot q'^2 + \frac{m^2\omega_1^2}{\hbar^2}\chi^{ro}(\underset{\sim}{q}', \omega_1).$$

Similarly, $\sum_{\underset{\sim}{k}\sigma} (\underset{\sim}{k}\cdot\underset{\sim}{q})^2 \chi^{co}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}', \omega_1) = -\frac{mn}{\hbar^2} q'^2 + \frac{m^2\omega_1^2}{\hbar^2}\chi^{co}(\underset{\sim}{q}', \omega_1)$.

Hence, $\mathrm{Im} \sum_{\underset{\sim}{k}\sigma}{}' (\underset{\sim}{k}\cdot\underset{\sim}{q})^2 F^{(1)}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},\underset{\sim}{q}',-\omega)$

$$= v(\underset{\sim}{q}-\underset{\sim}{q}')\frac{\pi}{4}\int_0^\infty d\omega_1 \Bigg[\frac{q^2}{2}\left(1-(\hat{q}\cdot\hat{q}')^2\right)q_F^2\cdot\Bigg\{\mathrm{Im}\left(\frac{\sum_{\underset{\sim}{k}\sigma} k^2 x^{c}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega_1,-\omega)}{\epsilon^{c}(\underset{\sim}{q}',\omega_1,-\omega)}\right)x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)$$

$$- x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega+\omega_1)\,\mathrm{Im}\left(\frac{\sum_{\underset{\sim}{k}\sigma} k^2 x^{r}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega_1)}{\epsilon^{r}(\underset{\sim}{q}',\omega_1)}\right)\Bigg\}$$

$$+\frac{q^2}{2q'^2}\left(3(\hat{q}\cdot\hat{q}')-1\right)\frac{m^2}{\hbar^2}\Big\{(\omega_1-\omega)^2 x^{c\prime\prime}(\underset{\sim}{q}',\omega_1-\omega)\,x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)$$

$$-\omega_1^2\, x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega+\omega_1)\,x^{r\prime\prime}(\underset{\sim}{q}',\omega_1)\Big\}$$

$$-\frac{q^2}{2q'^2}\left(3(\hat{q}\cdot\hat{q}')-1\right)\frac{m}{\hbar^2}\Big\{x^{c\prime\prime}(\underset{\sim}{q}',\omega_1-\omega)\,x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega_1)$$

$$- x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega+\omega_1)\,x^{r\prime\prime}(\underset{\sim}{q}',\omega_1)\Big\}\Bigg]$$

$$= v(\underset{\sim}{q}-\underset{\sim}{q}')\frac{q^2}{2}\frac{\pi}{4}\Bigg[q_F^2\left\{1-(\hat{q}\cdot\hat{q}')^2\right\}\int_0^\omega d\omega_1\, x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1)\,\mathrm{Im}\left(\frac{\sum_{\underset{\sim}{k}\sigma} k^2 x^{r}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}',\omega_1)}{\epsilon^{r}(\underset{\sim}{q}',\omega_1)}\right)$$

$$+\frac{1}{q'^2}\cdot\frac{m^2}{\hbar^2}\left\{3(\hat{q}\cdot\hat{q}')^2-1\right\}\int_0^\omega d\omega_1\,\omega_1^2\, x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1)\,x^{r\prime\prime}(\underset{\sim}{q}',\omega_1)$$

$$-\frac{m}{\hbar^2 q'^2}\left\{3(\hat{q}\cdot\hat{q}')^2-1\right\}\int_0^\omega d\omega_1\, x^{r\prime\prime}(\underset{\sim}{q}-\underset{\sim}{q}',\omega-\omega_1)\,x^{r\prime\prime}(\underset{\sim}{q}',\omega_1)\Bigg]. \qquad (A.5.3)$$

APPENDIX VI

The density operator $\hat{\rho}(\underset{\sim}{q},t)$ is given by,

$$\hat{\rho}(\underset{\sim}{q},t) = \sum_{\underset{\sim}{k}\sigma} a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}(t)\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}(t) = \sum_{\underset{\sim}{k}\sigma} \hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t).$$

The variation from equilibrium of this operator is denoted by $\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t)$. Thus

$$\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) = \hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q},t) - \langle \hat{\rho}_{\underset{\sim}{k}\sigma}(q)\rangle_{eq}.$$

We wish to evaluate the commutators of these operators and also obtain the values at equilibrium. We start with,

$$\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})\,\hat{\rho}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') = a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\, a^{+}_{\underset{\sim}{k}'-\underset{\sim}{q}'/2\sigma'}\, a_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'}$$

$$= a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2+\underset{\sim}{q}'\sigma}\, \delta_{\underset{\sim}{k}'\sigma',\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{q}')/2\sigma}$$

$$- a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2-\underset{\sim}{q}'\sigma}\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma}\, \delta_{\underset{\sim}{k}',\underset{\sim}{k}-(\underset{\sim}{q}+\underset{\sim}{q}')/2}\, \delta_{\sigma\sigma'}$$

$$+ a^{+}_{\underset{\sim}{k}'-\underset{\sim}{q}/2\sigma'}\, a_{\underset{\sim}{k}'+\underset{\sim}{q}'/2\sigma'}\, a^{+}_{\underset{\sim}{k}-\underset{\sim}{q}/2\sigma}\, a_{\underset{\sim}{k}+\underset{\sim}{q}/2\sigma},$$

using the anticommutation properties of $a_{\underset{\sim}{k}\sigma}$ and $a^{+}_{\underset{\sim}{k}\sigma}$.

Then we have the commutation relation,

$$\left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}),\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}')\right]_{-}$$

$$= \delta_{\sigma\sigma'}\left[\delta_{\underset{\sim}{k}',\underset{\sim}{k}+(\underset{\sim}{q}+\underset{\sim}{q}')/2}\, \hat{\rho}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}') - \delta_{\underset{\sim}{k}',\underset{\sim}{k}-(\underset{\sim}{q}+\underset{\sim}{q}')/2}\, \hat{\rho}_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}')\right]. \quad (A\cdot 6\cdot 1)$$

Using this relation, we have,

$$\left[\hat{\tilde{\rho}}(q),\, \hat{\tilde{\rho}}(q')\right]_{-} = \sum_{\substack{\underset{\sim}{k}\sigma \\ \underset{\sim}{k}'\sigma'}} \left[\hat{\tilde{\rho}}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q}),\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}')\right]_{-}$$

$$= \sum_{k\sigma}\left[\hat{\rho}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}') - \hat{\rho}_{\underset{\sim}{k}-\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}')\right] = 0. \quad (A\cdot 6\cdot 2)$$

Thus we see that $\hat{\rho}(\underset{\sim}{q})$ are boson like operators that commute with each other. The operators $\hat{\rho}_{\underset{\sim}{k}\sigma}(\underset{\sim}{q})$ however do not commute as is shown in (A.6.1). From equation (A.6.1) we also have,

$$[\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q}),\hat{\tilde{\rho}}(\underline{q}')] = \sum_{\underline{k}'\sigma'}[\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q}),\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}')]_- ,$$

$$= \hat{\rho}_{\underline{k}+\underline{q}'/2\sigma}(\underline{q}+\underline{q}') - \hat{\rho}_{\underline{k}-\underline{q}'/2\sigma}(\underline{q}+\underline{q}') . \qquad (A.6.4)$$

When we work with higher order correlation functions we need to evaluate commutators involving more number of density operators, e.g.,

$$\langle[\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})\,\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}'),\hat{\tilde{\rho}}(-\underline{q}-\underline{q}')]_-\rangle_{eq}$$

$$= \langle\{\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})[\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}'),\hat{\tilde{\rho}}(-\underline{q}-\underline{q}')]_- + [\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q}),\hat{\tilde{\rho}}(-\underline{q}-\underline{q}')]_-\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}')\}\rangle_{eq},$$

$$= \langle[\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})\{\hat{\rho}_{\underline{k}'-(\underline{q}+\underline{q}')/2\sigma'}(-\underline{q}) - \hat{\rho}_{\underline{k}'+(\underline{q}+\underline{q}')/2\sigma'}(-\underline{q})\}$$

$$+\{\hat{\rho}_{\underline{k}-(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}') - \hat{\rho}_{\underline{k}+(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}')\}\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}')]\rangle_{eq},$$

$$= \langle[\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})\{\hat{\tilde{\rho}}_{\underline{k}'-(\underline{q}+\underline{q}')/2\sigma'}(-\underline{q}) - \hat{\tilde{\rho}}_{\underline{k}'+(\underline{q}+\underline{q}')/2\sigma'}(-\underline{q}) + \delta_{\underline{q},0}(n_{\underline{k}'-\underline{q}'/2\sigma'} - n_{\underline{k}'+\underline{q}'/2\sigma'})\}$$

$$+\{\hat{\tilde{\rho}}_{\underline{k}-(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}') - \hat{\tilde{\rho}}_{\underline{k}+(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}') + \delta_{\underline{q},0}(n_{\underline{k}-\underline{q}/2\sigma} - n_{\underline{k}+\underline{q}/2\sigma})\}\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}')]\rangle_{eq},$$

$$= \langle\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})\,\hat{\tilde{\rho}}_{\underline{k}'-(\underline{q}+\underline{q}')/2\sigma'}(-\underline{q})\rangle_{eq} - \langle\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})\,\hat{\tilde{\rho}}_{\underline{k}'+(\underline{q}+\underline{q}')/2\sigma'}(-\underline{q})\rangle_{eq}$$

$$+\langle\hat{\tilde{\rho}}_{\underline{k}-(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}')\,\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}')\rangle_{eq} - \langle\hat{\tilde{\rho}}_{\underline{k}+(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}')\,\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(+\underline{q}')\rangle_{eq}$$

(A.6.4)

because,

$$\langle\hat{\tilde{\rho}}_{\underline{k}\sigma}(\underline{q})\rangle_{eq} = \langle\hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}')\rangle_{eq} = 0$$

For still higher order functions we use the following scheme of decoupling

$$\langle [ABC, D]_- \rangle_{eq} = \langle AB \rangle_{eq} \langle [C, D]_- \rangle_{eq}$$
$$+ \langle AC \rangle_{eq} \langle [B, D]_- \rangle_{eq} + \langle BC \rangle_{eq} \langle [B, D]_- \rangle_{eq} .$$

Then,

$$\frac{\Theta(t)}{i\hbar V} \Big\langle \Big[\hat{\tilde{\rho}}(\underset{\sim}{q}_1, t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1, t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$= \frac{\Theta(t)}{i\hbar V} \langle \hat{\tilde{\rho}}(\underset{\sim}{q}_1, t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1, t) \rangle_{eq} \Big\langle \Big[\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$+ \frac{\Theta(t)}{i\hbar V} \langle \hat{\tilde{\rho}}(\underset{\sim}{q}_1, t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \rangle_{eq} \Big\langle \Big[\hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1, t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$+ \frac{\Theta(t)}{i\hbar V} \langle \hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(\underset{\sim}{q}-\underset{\sim}{q}_1, t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \rangle_{eq} \Big\langle \Big[\hat{\tilde{\rho}}(\underset{\sim}{q}_1, t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$= \frac{\Theta(t)}{i\hbar V}\, \delta_{\underset{\sim}{q},0} \langle \hat{\tilde{\rho}}(\underset{\sim}{q}_1, t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1, t) \rangle_{eq} \Big\langle \Big[\hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$+ \frac{\Theta(t)}{i\hbar V}\, \delta_{\underset{\sim}{q}_1+\underset{\sim}{q}',0} \langle \hat{\tilde{\rho}}(-\underset{\sim}{q}', t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \rangle_{eq} \Big\langle \Big[\hat{\tilde{\rho}}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma}(\underset{\sim}{q}+\underset{\sim}{q}', t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$+ \frac{\Theta(t)}{i\hbar V}\, \delta_{\underset{\sim}{q}_1, \underset{\sim}{q}+\underset{\sim}{q}'} \Big\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}-(\underset{\sim}{q}+\underset{\sim}{q}')/2\sigma}(-\underset{\sim}{q}', t)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}', t) \Big\rangle_{eq}$$
$$\cdot \Big\langle \Big[\hat{\tilde{\rho}}(\underset{\sim}{q}+\underset{\sim}{q}', t)\, ,\, \hat{\tilde{\rho}}(-\underset{\sim}{q}-\underset{\sim}{q}', 0) \Big]_- \Big\rangle_{eq}$$

$$= \delta_{\underset{\sim}{q},0} \langle \hat{\tilde{\rho}}(\underset{\sim}{q}_1)\, \hat{\tilde{\rho}}_{\underset{\sim}{k}-\underset{\sim}{q}_1/2\sigma}(-\underset{\sim}{q}_1) \rangle_{eq} \sum_{\underset{\sim}{k}_1\sigma_1} \chi^{\nu}_{\underset{\sim}{k}'\sigma', \underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}', t)$$

$$+ \delta_{\underset{\sim}{q}_1+\underset{\sim}{q}',0} \Big\langle \hat{\tilde{\rho}}(-\underset{\sim}{q}')\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \Big\rangle_{eq} \sum_{\underset{\sim}{k}_1\sigma_1} \chi^{\nu}_{\underset{\sim}{k}+\underset{\sim}{q}'/2\sigma\, \underset{\sim}{k}_1\sigma_1}(\underset{\sim}{q}+\underset{\sim}{q}', t)$$

$$+ \delta_{\underset{\sim}{q}_1, \underset{\sim}{q}+\underset{\sim}{q}'} \Big\langle \hat{\tilde{\rho}}_{\underset{\sim}{k}-(\underset{\sim}{q}+\underset{\sim}{q}')/2\sigma'}(-\underset{\sim}{q}')\, \hat{\tilde{\rho}}_{\underset{\sim}{k}'\sigma'}(\underset{\sim}{q}') \Big\rangle_{eq} \chi^{\nu}(\underset{\sim}{q}+\underset{\sim}{q}', t)$$

(A.6.5)

Similarly we have,

$$\frac{\Theta(t)}{i\hbar V} \left\langle \left[\hat{\tilde{\rho}}_{\underline{k}-\underline{q}_1/2\sigma}(\underline{q}-\underline{q}_1,t)\, \hat{\tilde{\rho}}(\underline{q}_1,t)\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}',t),\ \hat{\tilde{\rho}}(-\underline{q}-\underline{q}',0) \right]_- \right\rangle_{eq}$$

$$= \delta_{\underline{q},0} \left\langle \hat{\tilde{\rho}}_{\underline{k}-\underline{q}_1/2\sigma}(-\underline{q}_1)\, \hat{\tilde{\rho}}(\underline{q}_1) \right\rangle_{eq} \sum_{\underline{k},\sigma_1} \chi^r_{\underline{k}'\sigma',\underline{k},\sigma_1}(\underline{q}',t)$$

$$+ \delta_{\underline{q}_1,\underline{q}+\underline{q}'} \left\langle \hat{\tilde{\rho}}_{\underline{k}-(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}')\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}') \right\rangle_{eq} \chi^r(\underline{q}+\underline{q}',t)$$

$$+ \delta_{\underline{q}+\underline{q}',0} \left\langle \hat{\tilde{\rho}}(\underline{q}')\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}') \right\rangle_{eq} \sum_{\underline{k},\sigma_1} \chi^r_{\underline{k}+\underline{q}'/2\sigma\ \underline{k},\sigma_1}(\underline{q}+\underline{q}',t) \qquad (A.6.6)$$

$$\frac{\Theta(t)}{i\hbar V} \left\langle \left[\hat{\tilde{\rho}}(\underline{q}_1,t)\, \hat{\tilde{\rho}}_{\underline{k}+\underline{q}_1/2\sigma}(\underline{q}-\underline{q}_1,t)\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}',t),\ \hat{\tilde{\rho}}(-\underline{q}-\underline{q}',0) \right]_- \right\rangle_{eq}$$

$$= \delta_{\underline{q},0} \left\langle \hat{\tilde{\rho}}(\underline{q}_1)\, \hat{\tilde{\rho}}_{\underline{k}+\underline{q}_1/2\sigma}(-\underline{q}_1) \right\rangle_{eq} \sum_{\underline{k},\sigma_1} \chi^r_{\underline{k}'\sigma',\underline{k},\sigma_1}(\underline{q}',t)$$

$$+ \delta_{\underline{q}+\underline{q}',0} \left\langle \hat{\tilde{\rho}}(-\underline{q}')\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}') \right\rangle_{eq} \sum_{\underline{k},\sigma_1} \chi^r_{\underline{k}-\underline{q}'/2\sigma\ \underline{k},\sigma_1}(\underline{q}+\underline{q}',t)$$

$$+ \delta_{\underline{q}_1,\underline{q}+\underline{q}'} \left\langle \hat{\tilde{\rho}}_{\underline{k}+\frac{(\underline{q}+\underline{q}')}{2}\sigma}(-\underline{q}')\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}') \right\rangle_{eq} \chi^r(\underline{q}+\underline{q}',t). \qquad (A.6.7)$$

$$\frac{\Theta(t)}{i\hbar V} \left\langle \left[\hat{\tilde{\rho}}_{\underline{k}+\underline{q}_1/2\sigma}(\underline{q}-\underline{q}_1,t)\, \hat{\tilde{\rho}}(\underline{q}_1,t)\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}',t),\ \hat{\tilde{\rho}}(-\underline{q}-\underline{q}',0) \right]_- \right\rangle_{eq}$$

$$= \delta_{\underline{q},0} \left\langle \hat{\tilde{\rho}}_{\underline{k}+\underline{q}_1/2\sigma}(-\underline{q}_1)\, \hat{\tilde{\rho}}(\underline{q}_1) \right\rangle_{eq} \sum_{\underline{k},\sigma_1} \chi^r_{\underline{k}'\sigma',\underline{k},\sigma_1}(\underline{q}',t)$$

$$+ \delta_{\underline{q}_1,\underline{q}+\underline{q}'} \left\langle \hat{\tilde{\rho}}_{\underline{k}+(\underline{q}+\underline{q}')/2\sigma}(-\underline{q}')\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}') \right\rangle_{eq} \chi^r(\underline{q}+\underline{q}',t)$$

$$+ \delta_{\underline{q}+\underline{q}',0} \left\langle \hat{\tilde{\rho}}(-\underline{q}')\, \hat{\tilde{\rho}}_{\underline{k}'\sigma'}(\underline{q}') \right\rangle_{eq} \sum_{\underline{k},\sigma_1} \chi^r_{\underline{k}-\underline{q}'/2\sigma\ \underline{k},\sigma_1}(\underline{q}+\underline{q}',t). \qquad (A.6.8)$$

REFERENCES

1. P.C. Martin, in 'Many Body Physics', eds. : C. deWitt and R. Balian, Gordon and Breach, New York (1968).
2. K.S. Singwi and M.P. Tosi, in 'Solid State Physics', Vo.36,eds. : H. Ehrenreich, F. Seitz and D. Turnbull, Academic Press (1981) ; and references therein.
3. S. Ichimaru, Rev. Mod. Phys. 54, 1017 (1982) ; and references therein.
4. H. Raether, in 'Excitations of plasmons and interband transitions by electrons ', Springer Tracts in Modern Physics, Vol.88, ed. : G. Hohler, Springer-Verlag,Berlin (1980).
5. J.P. Hansen and I.R. McDonald, in 'Theory of simple liquid', Academic Press, London (1976)..
6. K.S. Singwi, A. Sjölander, M.P. Tosi and R.H. Land, Phys.Rev. B1, 1044 (1970).
7. D.F. Dubois and M.G. Kivelson, Phys.Rev.186, 409 (1969).
8. G. Niklasson, Phys.Rev., B10, 3052 (1974).
9. A. Holas, P.K. Aravind and K.S. Singwi, Phys.Rev. B20, 4912 (1979).
10. P.K. Aravind, A. Holas and K.S. Singwi, Phys.Rev. B25, 561 (1982).
11. G.D. Mahan, in 'Antwerp Advanced Study Institute on Elementary Excitations in Solids, Molecules and Atoms', Part B, eds. : J.T. Devereese, A.B. Kunz and T.C. Collins, Plenum, New York (1974).
12. Chayanika Shah and G. Mukhopadhyay, Solid State Commun. 48, 1035 (1983).

13. R. Ray and G.D. Mahan, Phys.Lett. 42A, 301 (1972).

14. A. Shih and V.A. Parsegian, Phys.Rev. A12, 835 (1975).

15. A. Lunz, L. Mattera, M. Rocca, F. Tommasini and U.Valbusa, Surf.Sci. 120, L447 (1982).

16. D. Langebin, in 'Theory of Van der Waals attraction', Springer, New York (1974) ; and references therein.

17. R. Kubo, Rep.Prog.Phys. 29, 255 (1966).

18. J. des Cloizeaux, in 'Lectures on Theory of Condensed Matter prsented at an international course, Trieste', International Atomic Energy Agency, Vienna (1968).

19. D. Pines and P. Noziéres, in 'The Theory of Quantum Fluids', Benjamin, New York (1966).

20. L. van Hove, Phys.Rev. 95, 249 (1954).

21. R.D. Puff, Phys.Rev. 137, A406 (1965).

22. K.N. Pathak and P. Vashishta, Phys.Rev.B7, 4300 (1973).

23. D. Forster, P.C. Martin and S. Yip, Phys.Rev. 170, 155 (1968).

24. F. Family, Phys.Rev.Lett. 36, 1374 (1975)

25. J.M. Luttinger and P. Noziéres, Phys.Rev. 127, 1423 (1962) ; 127, 1431 (1962).

26. P. Vashishta and K.S. Singwi, Phys.Rev. B6, 275 (1972).

27. J. Lindhard, Mat.Fys.Medd.-K.Dan.Vidensk.Selsk. 28, 1 (1954).

28. J. Hubbard, Proc.Royal Soc.London Ser. A240, 539(1957) ; 243, 336 (1957).

29. P. Noziéres, in 'Theory of Interacting Systems', Benjamin, New York (1964).

30. D.J.W. Geldart and S.H. Vosko, Can.J.Phys. 44, 2137 (1966).

31. K.S. Singwi, M.P. Tosi, R.H. Land and A. Sjölander, Phys.Rev. 176, 589 (1968).

32. P. Vashishta and K.S. Singwi, Phys.Rev. B6, 875 (1972) ; K.N. Pathak and P. Vashishta, Phys.Rev. B7, 3649 (1973).

33. S. Ichimaru, in 'Basic Principles of Plasma Physics', Benjamin, Reading, Mass.(1973).

34. A.K. Gupta and K.S. Singwi, Phys.Rev. B15, 1801(1977).

35. J.S. Vaishya and A.K. Gupta, Phys.Rev. B7, 4300 (1973).

36. H. Totsuji and S. Ichimaru, Prog.Theor.Phys. 50, 753 (1973) ; 52, 42 (1974).

37. D.J.W. Geldart and R. Taylor, Can.J.Phys. 48, 155 (1970); 48, 167 (1970).

38. D.J.W. Geldart, Can.J.Phys. 45, 3139 (1967).

39. P.M. Platzman and P. Eisenberger, Phys.Rev.Lett. 33, 152 (1974).

40. P. Zacharias, J.Phys. F5, 645 (1975).

41. F. Toigo and T.O. Woodruff, Phys.Rev. B2, 3958 (1970) ; B4, 371 (1971).

42. F. Brosens, L.F. Lemmens and J.T. Devreese, Phys. Status Solidi B74, 45 (1976) ; F. Brosens, J.T. Devreese and L.F. Lemmens, Phys. Status Solidi B 80, 99 (1977).

43. J.T. Devreese, F. Brosens and L.F. Lemmens, Phys.Rev. B21, 1349 (1980) ; F. Brosens, J.T. Devreese and L.F. Lemmens, Phys.Rev. B21, 1363 (1980).

44. D.N. Tripathy and S.S. Mandal, Phys.Rev. B16, 231 (1977) ; S.S. Mandal, B.K. Rao and D.N. Tripathy, Phys.Rev. B18, 2524 (1978) ; D.N. Tripathy and R.K. Pal, Phys.Status Solidi B104, 345 (1981).

45. M.W.C. Dharma-wardana, J.Phys. C9, 1919 (1976).

46. T. Hasegawa and M. Shimizu, J.Phys.Soc.Japan 38, 965 (1975).

47. K. Utsumi and S. Ichimaru, Phys.Rev. B22, 1522 (1980) ; B22, 5203 (1980) ; B23, 3291 (1981) ; A26, 603 (1981).

48. G. Mukhopadhyay, R.K. Kalia and K.S. Singwi, Phys.Rev. Lett. 34, 950 (1975).

49. K. Awa, H. Yasuhara and T. Asahi, Solid State Commun. 38, 1285 (1981) ; Phys.Rev. B25, 3670 (1982) ; Phys. Rev. B25, 3687 (1982).

50. G. Niklasson, A. Sjolander and F. Yoshida, J.Phys.Soc.Japan 52, 2140 (1983).

51. F. Green, D.N. Lowy and J. Szymánski, Phys.Rev.Lett. 48, 638 (1982).

52. D.N. Lowy and G.E. Brown, Phys.Rev. B12, 2138 (1975).

53. H. Mori, Prog.Theor.Phys. 33, 423 (1965) ; 34, 399 (1965).

54. M. Nusair and B. Goodman, Phys.Lett. 70A, 275 (1979).

55. V.K. Jindal, H.B. Singh and K.N. Pathak, Phys.Rev. B15, 252 (1977).

56. G. Mukhopadhyay and A. Sjölander, Phys.Rev. B17, 3589 (1978).

57. H. De Raedt and B. De Raedt, Phys.Rev. B18, 2039 (1978).

58. F. Yoshida, S. Takeno and H. Yasuhara, Prog.Theor.Phys. 64, 40 (1980).

59. A. Sharma, M.R. Monga and K.N. Pathak, Solid State Commun. 36, 253 (1980).

60. Chayanika Shah and G. Mukhopadhyay, Solid State Commun. 52, 627 (1984).

61. D.F. Dubois, Ann.Phys. 8, 24 (1959).

62. G.D. Mahan, Phys.Rev. B5, 739 (1972).

63. A.A. Lucas, Phys.Rev. B4,2939 (1971).

64. R.H. Ritchie, Phys.Lett. 38A, 189 (1972).

65. P.J. Feibelman, Surf.Sci. 27, 438 (1971).

66. A.A. Lucas, in 'Antwerp Advanced Study Institute on Elementary excitations in solids, molecules and atoms', Part A, eds. : J.T. Devreese, A.B. Kunz and T.C. Collins, Plenum, New York (1974).

67. M. Sunjic, G. Toulose and A.A. Lucas, Solid State Commun. 11, 1629 (1972).

68. B. Gumhalter, J. de Physique (Paris) 38, 1117 (1977).

69. D.M. Newns, Phys.Rev. B1, 3304 (1970).

70. J. Heinrichs, Phys.Rev. B8, 1346 (1973).

71. J. Harris and R. Jones, J. Phys. C6, 3585 (1973).

72. W. Ekardt, Phys.Rev. B28, 1099 (1983).

73. A. Puri and W.L. Schaiach, Phys.Rev. B28, 1781 (1983).

74. G. Mukhopadhyay and S. Lundqvist, Physica Scripta 17, 69 (1978).

75. P.R. Rao, Chayanika Shah and G. Mukhopadhyay, Pramana 23, 119 (1984).

76. S.Q. Wang and G.D. Mahan, Phys.Rev. B6, 4517 (1972).

77. A.A. Lucas and E. Kartheuser, Phys.Rev. B1, 3588 (1970).

78. A.A. Lucas, E. Kartheuser and R.G. Badro, Phys.Rev. B2, 2488 (1970).

79. W. Gautschi and W.F. Cahill, in 'Handbook of Mathematical Functions', eds. : M. Abramowitz and I. Stegun, Dover, New York (1970).

80. G. Mukhopadhyay, Solid State Commun. 28, 277 (1978).

81. P.R. Rao, Ph.D. Thesis to be submitted, IIT Bombay (1985).

82. R.H. Ritchie and A.L. Marusak, Surf.Sci. 4, 234 (1966).

83. A. Shih, D. Raskin and P. Kusch, Phys.Rev. A9, 652 (1974).

84. A. Shih, Phys.Rev. A9, 1507 (1974).

85. G. Mukhopadhyay and J. Mahanty, Solid State Commun. 16, 597 (1975).

86. E. Zaremba and W. Kohn, Phys.Rev. B13, 2270 (1976).

87. M.J. Mehl and W.L. Schaich, Surf.Sci. 99, 553 (1980).

88. J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, in 'Molecular Theory of Gases and Liquids', Chapter 12, John Wiley and Sons Inc., New York (1954).

89. J. Bardeen, Phys.Rev. B58, 727 (1940).

90. F. Delanaye, A. Lucas and G.D. Mahan, Surf.Sci. 70, 629 (1978).

91. G. Somorjai, in 'Principles of Surface Chemistry', Page 192, Prentice-Hall (1972).

ACKNOWLEDGEMENTS

Reaching this stage has been a long task and a lot of people have contributed directly or indirectly to it, all of whom I would like to thank profusely.

A very big 'thank-you' to Dr. Gautam Mukhopadhyay, my guide, without whose help and encouragement this work would not have reached this stage.

A special thanks to Raghu also for everything that he has done.

Chayanika

SUMMARY

This thesis consists of two parts, where the first part deals with dynamical many body effects in a homogeneous electron system, while the second part deals with the dynamical response in inhomogeneous electron system, in particular, a metallic system represented by a semi-infinite jellium.

In the first part, we developed a formulation, for a frequency and wavevector dependent dielectric function, which incorporates the dynamics of the exchange-correlation hole around each electron in a homogeneous electron gas system. We followed the equation of motion approach where we truncated the series of coupled equations at the equation of motion for the one particle Wigner distribution function by decoupling the two particle function occurring therein (viz., $f^{(2)} = f^{(1)}f^{(1)}C^{(2)}/n^2$) via the function

$$C^{(2)}(\underset{\sim}{r},\underset{\sim}{r}',t) = \sum_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'} f^{(2)}_{\underset{\sim}{k}\sigma\underset{\sim}{k}'\sigma'}(\underset{\sim}{r},\underset{\sim}{r}',t).$$

The resulting integral equation was then solved using the various approximations for $\bar{C}^{(2)}$ (or $\bar{D}^{(2)}$, the density-density correlation function which is related to $\bar{C}^{(2)}$).

It was seen that simple approximations for $\bar{C}^{(2)}$ led to earlier results obtained using different approaches, thus

providing a simple, systematic method for obtaining the earlier results. For an improved treatment we made an ad-hoc SSTL[6] like approximation for the vertex function occurring in the integral equation for the corresponding time-ordered function and obtained a frequency dependent local field correction. This local field could be split into two parts. One was a static term obtained earlier by Singwi et al. (STLS)[31] which gave good results in the static limit. The other was a complex, frequency dependent term whose imaginary part had a frequency dependence controlled by the coupling between the excitation modes of the system. Such a feature had been observed earlier by Sharma et al. who used the Mori formalism. This mode coupling had not been noticed in any of the earlier equation of motion approaches. The results for the damping coefficient γ of the long wavelength plasmons in this case compared fairly well with the perturbative calculations in the weak coupling limit. The values for γ in the metallic density range were much smaller. The local field values for finite q and ω were found to exhibit many of the expected features. The double peak structure in the energy loss spectra, however, could not be observed. A drawback of this approximation was that the local field was found to have the same static and high frequency limits.

Attributing these failures to the ad-hoc nature of the approximation made for the vertex function, we improved

upon the approximation by using linear response theory to obtain the vertex function. The mode coupling feature was retained here too. Due to constraints on available computational facilities, it was not possible to carry out detailed numerical calculations (e.g. for dynamic structure factor) in this case. The value for γ in the $r_s \to 0$ limit here, however, compared very well with the perturbative results. The values of γ for r_s in the metallic density range were also higher than those calculated in the earlier approximation. To understand the content of this approximation we also developed a response function corresponding to $D^{(2)}$ in the presence of an external field and used its equation of motion to obtain $G(q,\omega)$. The local field was also obtained by extracting $\bar{C}^{(2)}$ using different approximations in the equation of motion for the two particle function. These two additional approaches indicated that the mode coupling feature present in our theory arose due to the inclusion of higher order correlations in our theory.

Another important aspect of the present work was in obtaining an expression for $f^{(2)eq}$, a hitherto unknown quantity. Numerical calculations were not attempted because of the heavy computational work involved.

In the second part of this thesis, we studied the interaction of a moving charge or atom (molecule) with a metal surface. Dynamic image potential $V(z,v)$ (due to a

moving charge interacting with the excitations at the metal surface) had been studied earlier assuming a constant speed of the charge. We included the acceleration of the charge and carried out self-consistent calculations for $V(z,v)$ and found that the inclusion of acceleration did not lead to much modification over the self-consistent local speed calculations suggested earlier (in an ad hoc manner) by Ray and Mahan[13]. We however showed how the local speed entered the theory in a natural way. Working within the model Hamiltonian approach we also calculated the dynamic interaction of an uniformly moving atom or molecule with a metal surface. Due to the large mass of the incoming particle it was found that the velocity was too small to show any significant effect on the interaction. We also studied the interaction of an atom or molecule with a layer of molecules adsorbed on a metal surface and found that from single loss probability measurements it could be possible to study the changes in the frequencies of adsorbed molecules.