INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

The Role of the Exchange and Correlation Term in the Lattice Dynamics of Alkali Metals.

by

Robert Blanchard

Submitted in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

Department of Physics,
Faculty of Pure and Applied Science,
University of Ottawa,
Ottawa, Canada

Approved for the Department of Physics

_____

Chairman

ACKNOWLEDGEMENTS

First and foremost I want to thank God who gave me the grace and strength to do this work.

Secondly, I wish to express my gratitude to Dr.Varshni for suggesting this subject to me and for making me acquainted with the field of Lattice Dynamics. I thankfully remember that he was always available for consultation.

I also wish to thank Mrs. van der Maas for so faithfully and conscientiously typing this thesis.

Finally I want to express my appreciation to the National Research Council for its financial support, and last but not least to my loving wife, who has been such an ideal and faithful companion throughout the time of my study.

STATEMENT OF ORIGINALITY

In chapter II the work of Hone (H60) is extended (the results are combined with those of Bailyn (B60)). A unified approach is given to the derivation of the "proton-electron" dielectric function, with simplifications achieved by the removal of certain unnecessary transformations.

In chapter III new derivations are given for the exchange and correlation terms obtained by several authors namely Toya (T58), Hubbard (H57), Geldart-Vosko (G65), Kleinman (K67) and Takahashi (T68). We then describe electron-electron screening in a more accurate way, and using a factorization procedure, new expressions for the exchange and correlation term are obtained.

In chapter IV the experimentally derived $G_E(Q)$ and $\int(Q)$ for rubidium are presented for the first time and the corresponding interatomic potential is calculated. Furthermore, a systematic study of model and empirical pseudopotentials is made with various expressions for the exchange and correlation term (some of them our own).

ABSTRACT

The contents of the present thesis can be described as follows. In chapter II the work of Hone (H60) is extended and the results are combined with those of Bailyn (B60). A unified approach is given to the derivation of the "proton-electron" dielectric function, with simplifications achieved by the removal of certain unnecessary transformations. A discussion of electron-electron screening shows why many of the results derived from Bailyn's and Hone's work are similar. In chapter III new derivations are given for the exchange and correlation terms obtained by several authors, namely Toya (T58), Hubbard (H57), Geldart-Vosko (G65), Kleinman (K67), and Takahashi (T68). We then show that electron-electron screening can be described in a more accurate way, and using a factorization procedure (introduced in chapter II), new expressions for the exchange and correlation term are obtained. In chapter IV we present the lattice dynamics of sodium, potassium and rubidium. Cochran's (C63) method of obtaining empirical effective potentials from the dispersion curves is discussed to obtain some insight into the problem. Then the method of Cowley et al (C66) is applied; a choice of the dielectric function is made, the pseudopotentials are determined and compared to those obtained by least squares fitting of different models. Finally, the dispersion curves are calculated and the interatomic potentials are also obtained.

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

The crystal dynamics of alkali metals has received considerable experimental and theoretical attention during the last few years. A large amount of experimental information on dispersion relations of frequency versus wave-vector has been obtained on sodium, potassium and more recently on rubidium and lithium. This has stimulated a number of theoretical studies. The main complexity in the problem originates from the interaction of conduction electrons with the ions that constitute the lattice.

The subject of lattice dynamics has been reviewed in recent years by de Launay (D56), Cochran (C63a) and by Joshi and Rajagopal (J68); standard reference works in the field are due to Born and Huang (B54) and by Maradudin, Montroll and Weiss (M63).

The theoretical models which have been used to investigate the lattice dynamics of alkali metals can be broadly classified in four categories.

(a) Born - von Karman Force Constant Models. The theory of such models is given in standard texts (B54, M63) and we shall not discuss them here.

(b) Phenomenological Models. Several authors have tried to take into account the effect of the electron gas in an approximate way.

In the phenomenological models of de Launay (D53, D54, D56),

Bhatia (B55a, B55b) and Sharma and Joshi (L63, S63b, S64) it is assumed that the conduction electrons behave like an ordinary gas, supporting a compressional but not a shearing stress. However, all of these models violate space group symmetry requirements (L65). Recently Krebs (K64, K65) has proposed a model in which the contributions of the ions to the elements of the dynamical matrix are the same as in a central force Born-von Karman model. The electronic contribution is calculated from a screened Coulomb interaction of the metal ions; the symmetry requirements are taken into account by including Umklapp processes. The theoretical dispersion curves for sodium are in good agreement with experiment. This model, however, suffers from a weakness: the derivative of the screened Coulomb interaction energy is not zero at equilibrium as it is for the Born-von Karman term. This result implies that external forces must be applied to maintain the system in equilibrium (Cochran C65a).

Recently Cheveau (C68a) has proposed a model which satisfies the requirement of translational invariance and is in equilibrium without recourse to external forces.

(c) First Principle Calculations. Toya was the first to perform a satisfactory calculation for the phonon frequencies in Na, taking into account the influence of the conduction electrons. He used the classic solution of the electron-phonon problem given by Bardeen (B37) in 1937, which was essentially based on the Wigner-Seitz model (W33) of the electron in a metal.

As is well known the frequencies of a monatomic lattice are obtained from the solutions of the secular equation

$$\left| D_{xy}(\vec{q}) - m\omega_j^2(\vec{q}) \right| = 0$$

where m is the mass of an ion.

Toya (T58a, T58) expressed the dynamical matrix $D_{xy}(\vec{q})$ as a sum of terms due to three different types of interactions

$$D_{xy}(\vec{q}) = C_{xy}(\vec{q}) + R_{xy}(\vec{q}) + E_{xy}(\vec{q})$$

where $C_{xy}(\vec{q})$ is the contribution from electrostatic forces between ions regarded as point charges, $R_{xy}(\vec{q})$ is the contribution from direct overlap or exchange repulsions between ion cores; and $E_{xy}(\vec{q})$ is the contribution of the conduction electrons, representing the effective ion-electron-ion interaction. Expressions for $C_{xy}(\vec{q})$ have been obtained by Kellermann (K40). These are summarized in Appendix E. For the core overlap interaction Toya assumed the Born-Mayer form:

$$V_R(r) = A \exp(-r/\rho)$$

where A and ρ are parameters. Then the expression for $R_{xy}(\vec{q})$ is

$$R_{xy}(\vec{q}) = (A/\rho)\sum_{\ell \neq 0} \exp(-\ell/\rho)\left\{-\delta_{xy}\ell^{-1} + (\rho^{-1} + \ell^{-1})(\ell_x\ell_y/\ell^2)\right\}\left[1-\exp(i\vec{q}\cdot\vec{\ell})\right]$$

Subsequently it was pointed out by Vosko (V64) that the contribution R_{xy} using the values of A and ρ as given by Born and Mayer, is probably too

big by a factor of about forty to one hundred.

For the contribution from the ion-electron-ion interaction, Toya derived the following expression

$$E_{xy}(\vec{q}) = -\frac{4\pi e^2}{v}\sum_{\tau}\frac{(q_x+\tau_x)(q_y+\tau_y)}{|\vec{q}+\vec{\tau}|^2}\,G^2(u)\,\mathscr{F}^{-1}(u)\,f(u)$$

where $\vec{\tau}$ is a reciprocal lattice vector.

Toya has included the term $\frac{4\pi e^2}{3v}\delta_{xy}$ in E_{xy}, we have included it in C_{xy}.

$$G(u) = \left\{1 + (V(r_s) - E_o)\,\frac{3u^2}{\beta E_F}\right\} g(2k_F r_s u)$$

$$\mathscr{F}(u) = \begin{cases} \frac{D_o}{D}\,\frac{2}{\beta}\,u^2 + (1 - Bu^2)f(u) & \text{for } Bu^2 < 1 \\ \frac{D_o}{D}\,\frac{2}{\beta}\,u^2 & \text{for } Bu^2 \geq 1 \end{cases}$$

$$f(u) = \frac{1}{2} + \frac{1-u^2}{4u}\,\ell n\left|\frac{1+u}{1-u}\right|$$

$$g(2k_F r_s u) = g(x) = 3(\sin x - x\cos x)/x^3$$

$$\beta = \frac{e^2 k_F}{\pi E_F}\,, \qquad E_F = \frac{\hbar^2 k_F^2}{2m'} \text{ is the Fermi energy}$$

$V(r_s)$ is the Hartree-Fock potential energy at the surface of the atomic sphere of radius r_s. D and D_o are the densities of states with and without exchange and correlation energies taken into account, B is a con-

stant introduced to take into account the effect of exchange and correlation interaction on the screening field.

Toya has used his method to calculate the dispersion curves (T58, T59) and thermal expansion (T61) of alkali metals. Toya's model has been used by Srivastava and Srivastava (S63a) to calculate the specific heat of sodium and potassium, and by Nutkins (N65) to calculate the effective calorimetric Debye temperature of sodium. Dayal and Srivastava (D64a) tried to improve the agreement of the results from Toya's theory with experiment for Na by multiplying the argument of the g function in the electron-ion term with a constant α nearly equal to unity. For sodium α was taken to be 1.04 (D64a) and for potassium 1.07 (S64a).

Toya used Slater's simplification (S51) for the exchange potential and made subsequent corrections to account for the reduction of density of states at the Fermi surface and for some other second order effects. To eliminate these somewhat uncertain corrections, Dayal and Srivastava (D65, S65a) have used Bailyn's (B60) matrix element for the electron-phonon interaction in place of Toya's in the Toya model. It was found that for sodium (D65) the resulting dispersion-curves were close to those obtained by Dayal and Srivastava (D64a) and were in good agreement with the experimental values.

Vosko, Taylor and Keech (V65) have treated the electron-ion term by the many body perturbation theory, the electron wave functions being approximated by single orthogonalized plane waves. Following Vosko (V64), the contribution due to the ion overlap was neglected. For a first principle calculation, the results for the dispersion curves of sodium obtained by these authors are quite reasonable.

(d) Method of Pseudopotentials. The method of pseudopotentials given by Phillips and Kleinmann (P59) and by Antoncik (A59) for the calculation of the band structure of metals has been employed in recent years to calculate the phonon frequencies in metals. The pseudopotential formalism and its applications have been reviewed by Sham and Ziman (S63), Ziman (Z64a) and by Harrison (H66). Sham (S65b) has developed the pseudopotential formalism for calculating the phonon frequencies in metals and has applied it to sodium. The pseudopotential, which arises from the orthogonalization of the wave functions of the conduction electrons to those of the core electrons has the effect of cancelling the Hartree-Fock potential near the ions. Sham showed that the resulting effective potential may be regarded as moving rigidly with the ions in the course of the lattice vibrations and within certain limits can be used to calculate the matrix element for the electron-phonon interaction, with the electrons represented by simple plane waves. The screening effects due to the interaction between electrons were considered in the Hartree-Fock approximation with a screened exchange potential. The results for the phonon dispersion curves were close to those obtained by Toya.

Cochran (C63) has analyzed the experimental results of Woods et al (W62) on the phonon dispersion relations in sodium and has found that the results are consistent with the concept of an effective potential. Cochran (C63) has also deduced this effective potential empirically and has found it to have qualitatively the form expected.

Cowley, Woods and Dolling (C66) have deduced this potential in a more rigorous way for sodium and potassium.

More recently Schneider and Stoll (S66, S66a), Animalu, Bonsignori

and Bortolani (A66), Ho (H67, H68), Shyu and Gaspari (S67, S68) and Ashcroft (A68) have investigated the lattice dynamics of alkali metals, using different pseudopotentials.

The contents of the present thesis will now be discussed. In chapter II the work of Hone (H60) is extended and the results are combined with those of Bailyn (B60). A unified approach is given to the derivation of the "proton-electron" dielectric function, with simplifications achieved by the removal of certain unnecessary transformations. A discussion of electron-electron screening shows why many of the results derived from Bailyn's and Hone's work are similar. In chapter III new derivations are given for the exchange and correlation terms obtained by several authors, namely Toya (T58), Hubbard (H57), Geldart-Vosko (G65), Kleinman (K67), and Takahashi (T68). We then show that electron-electron screening can be described in a more accurate way, and using a factorization procedure (introduced in chapter II), new expressions for the exchange and correlation term are obtained. In chapter IV we present the lattice dynamics of sodium, potassium and rubidium. Cochran's (C63) method of obtaining empirical effective potentials from the dispersion curves is discussed to obtain some insight into the problem. Then the method of Cowley et al (C66) is applied; a choice of the dielectric function is made, the pseudopotentials are determined and compared to those obtained by least squares fitting of different models. Finally, the dispersion curves are calculated and the interatomic potentials are also obtained.

CHAPTER II

Exchange and Correlation in Alkali Metals

1. Screened Impurities

We begin by considering the problem of electron screening in a gas of free electrons (Cochran, C65, p6). On introducing a small "imposed" charge +e, the electrons will pile up there in such a way that the field of the imposed charge is completely screened at large distance.

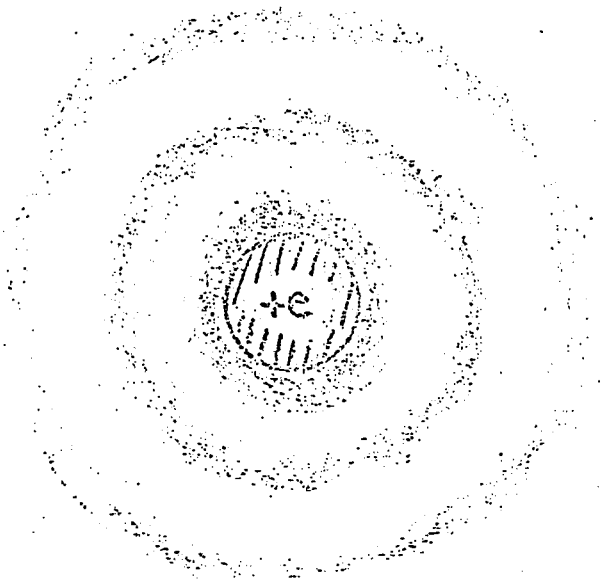


fig.(2.1)

To a first approximation the resulting potential is a screened Coulomb potential, which falls off exponentially with distance (Ziman, Z64, p131):

$$V_s(r) = \frac{e^2}{r} \exp(-k_s r) \qquad (2.1)$$

where k_s is the screening parameter, $1/k_s$ the screening "length". The Fourier transform of this potential can be written in such a way that the screening of the bare Coulomb potential is described by means of a dielectric constant $\varepsilon(Q)$, where $\vec{Q}$ is a general vector in reciprocal space. So let us write this result in the dielectric formulation.

The Coulomb potential $V_i(r) = \frac{e^2}{r}$

has the Fourier transform $V_i(Q) = \frac{4\pi e^2}{Q^2}$ *

We note the singularity at $Q = 0$ which corresponds to the infinite "range" of the Coulomb potential. The Fourier transform of the screened potential is

$$V_s(Q) = \frac{4\pi e^2}{Q^2 + k_s^2} \tag{2.2}$$

which may be written as

$$V_s(Q) = \frac{V_i(Q)}{\varepsilon(Q)} \tag{2.3}$$

where $\varepsilon(Q) = 1 + k_s^2/Q^2$ is the dielectric constant. Thus, the screened potential is the Coulomb potential divided by the dielectric constant. The singularity in $\varepsilon(Q)$ as $Q \to 0$ cancels out the singularity in $V_i(Q)$, removing the long-range part of the Coulomb interaction.

* A box of unit volume is assumed.

2. Scattering by a Potential V(r)

We consider an electron scattered by the potential V(r) (for example the screened potential for an impurity as shown in fig.(2.1)). Let $\vec{k}$ and $\vec{k}'$ be the initial and final wave vectors. In the Born approximation the rate of transition between the initial state Ψ_k and the final state $\Psi_{k'}$ is proportional to the square of the matrix element (Ziman, Z64, p51).

$$v_{kk'} = \int \Psi^*_{k'}(\vec{r})\ V\ (\vec{r})\ \Psi_k(\vec{r}) d^3\vec{r} \qquad (2.4)$$

We take these to be plane waves $\Psi_k = e^{i\vec{k}\cdot\vec{r}}$

thus $$v_{kk'} = \int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\ V(\vec{r}) d^3\vec{r} \qquad (2.5)$$

let $\vec{Q} = \vec{k} - \vec{k}'$ $$v_Q = \int e^{i\vec{Q}\cdot\vec{r}}\ V(\vec{r}) d^3\vec{r} \qquad (2.6)$$

This illustrates how the Fourier transform of a potential occurs naturally in a matrix element.

3. Scattering by lattice vibrations

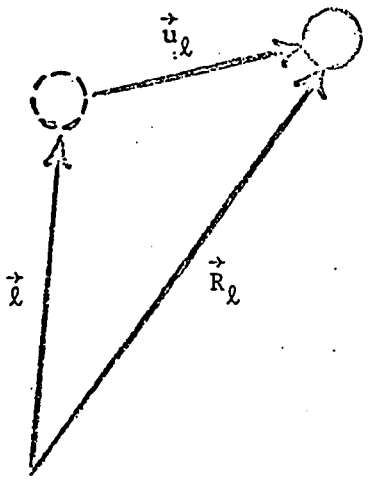
Consider a lattice where each atom is displaced from its equilibrium position. The potential $V(\vec{r})$ is a superposition of atomic potentials (Z64, p54).

$$V(\vec{r}) = \sum_{\ell} V_a(\vec{r} - \vec{R}_\ell) \qquad (2.7)$$

where $\vec{R}_\ell$ is the actual position of the atom (or ion) that ought to have been at the lattice site $\vec{\ell}$.

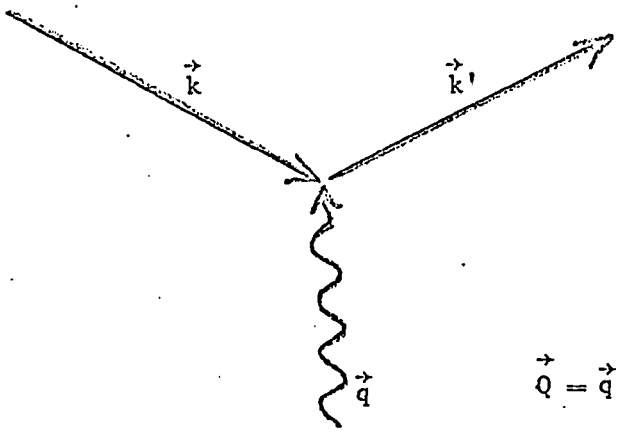
$$\vec{R}_\ell = \vec{\ell} + \vec{u}_\ell$$

$$= \vec{\ell} + \sum_{q} (\vec{U}_q e^{i\vec{q}\cdot\vec{r}} + \vec{U}_q^* e^{-i\vec{q}\cdot\vec{r}})$$



where $\vec{U}_q$ is the vector amplitude of the mode and $\vec{q}$ is the phonon wave-vector. The complex conjugate is included to make the displacement real. The matrix element for the scattering of an electron of initial and final wave-vector $\vec{k}$ and $\vec{k}'$ is given by (Z64, p57).

$$v_Q = -i\,\vec{Q} \cdot \vec{U}_q\, V_a(Q) \qquad (2.8)$$



$\vec{Q} = \vec{q}$ Normal process

where $\vec{Q} = \vec{q}$ for a Normal process

and $\vec{Q} = \vec{q} + \vec{\tau}$ for an Umklapp process

with $\vec{\tau}$ a reciprocal lattice vector.

We see that the Fourier transform of the atomic potential is involved in the matrix element.

4. Response of Electrons to Lattice Vibrations

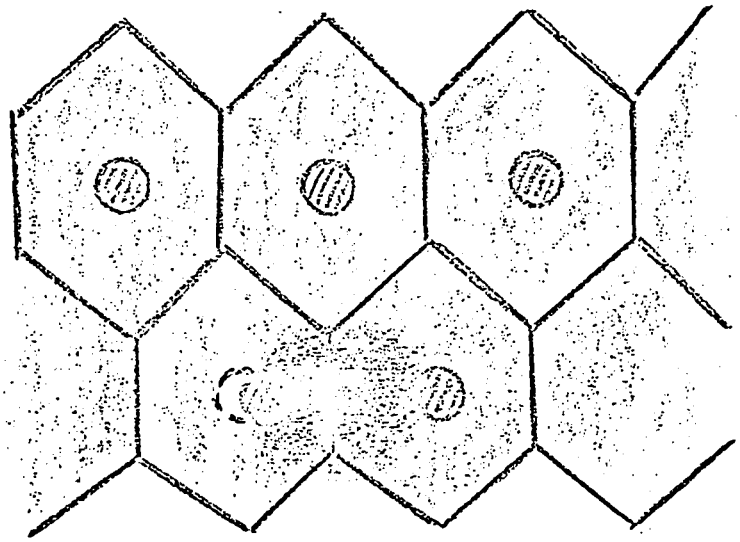


fig.(2.2)

In the case of metals it is often possible to identify a core of electrons that are tightly bound to the nuclei and essentially follow the nuclei in rigid motion. Outside the core there are nearly free electrons which move quite independently of the nuclei. Fig.(2.2) which is taken from ref. S65 represents a situation in which one ion is displaced from its equilibrium position. This leads to a change of the electron density around that ion and thus to a screening of the perturbing potential. Let $V_i(Q)$ be the Fourier transform of the perturbing potential. Then, in the Hartree approximation, the Fourier transform of the screened potential $V_s(Q)$ is given by (C65)

$$V_s(Q) = \frac{V_i(Q)}{\varepsilon(Q)} \tag{2.9}$$

where $$\varepsilon(Q) = 1 - \frac{8\pi e^2}{Q^2} \sum_{k'} \frac{n(\vec{k}' - \vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{2.10}$$

in which $$n(\vec{k}') = \begin{cases} 1 & \text{for } k' < k_F \\ 0 & \text{for } k' > k_F \end{cases}$$

and $E_{k'} = \frac{\hbar^2}{2m'} k'^2$ in the parabolic band approximation.

The integration over $\vec{k}'$ can be performed and eq.(2.10) yields

$$\varepsilon(Q) = 1 + \frac{\beta f(u)}{2u^2} \tag{2.11}$$

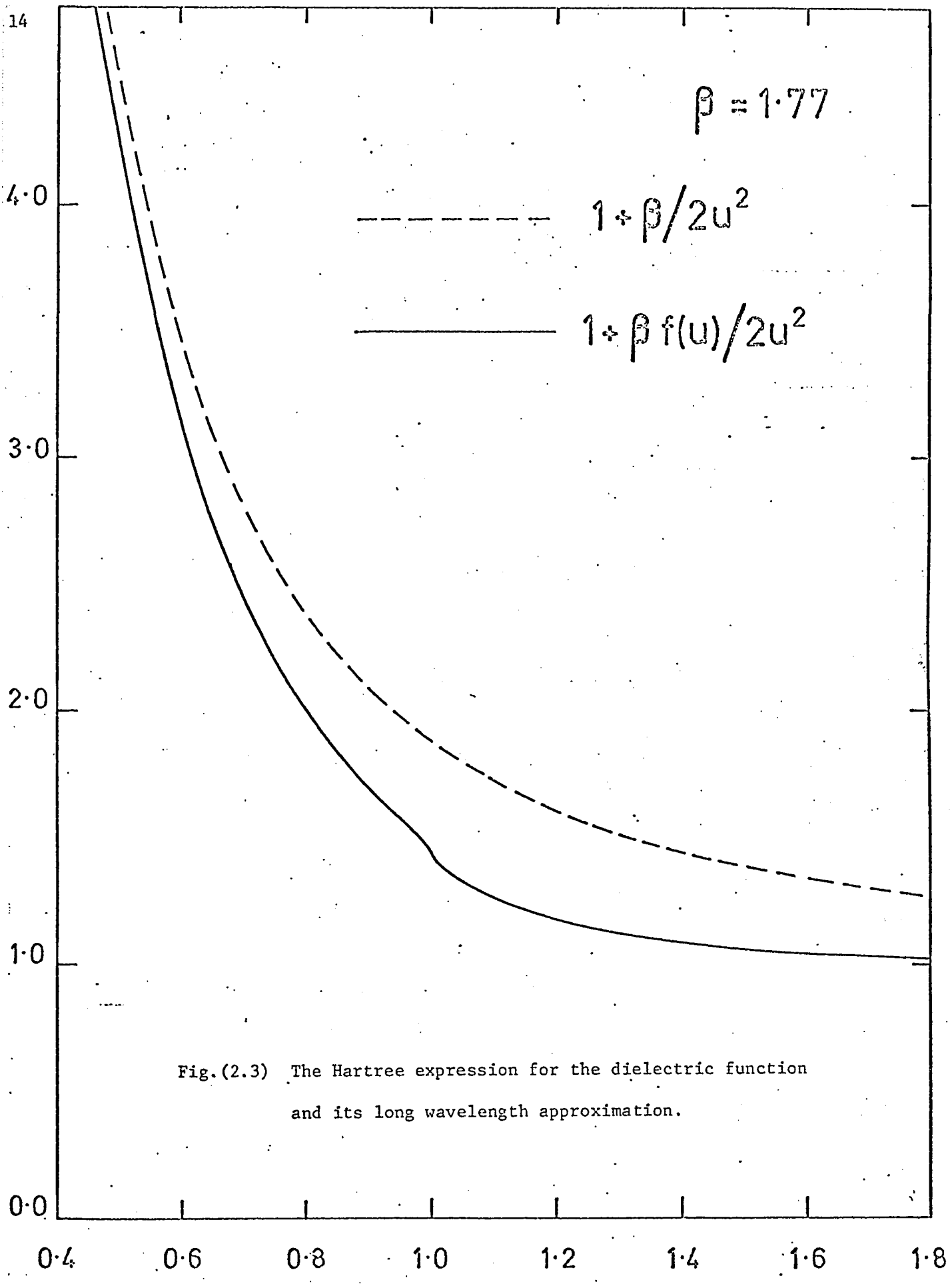


Fig.(2.3) The Hartree expression for the dielectric function and its long wavelength approximation.

where $f(u) = \frac{1}{2} + \frac{1 - u^2}{4u} \ln \left| \frac{1 + u}{1 - u} \right|$

$$u = Q/2k_F \quad \text{and} \quad \beta = 2/\pi a_o k_F$$

This result was obtained by Bardeen (B37). The long wavelength approximation to eq. (2.11) is obtained by noting that $f(o) = 1$ and by introducing the Thomas-Fermi screening parameter $k_s^2 = 2\beta k_F^2$, we get

$$\varepsilon(Q) = 1 + k_s^2 / Q^2 \qquad (2.12)$$

This expression is identical to the one obtained in the simple theory of screening (eq.(2.3)) where the screened potential is assumed to fall off exponentially with distance. Both the long wavelength and the Hartree approximation to $\varepsilon(Q)$ are plotted in fig.(2.3).

5. The Hartree Result in Bailyn's Notation

We rewrite the Hartree result in terms of the Bailyn notation (B60).

Let $v_Q^{\,i}$ represent the matrix element for the motion of the bare ions and v_Q the matrix element for the screened electron lattice interaction. Then Bailyn obtains the Hartree result in the form

$$v_Q = v_Q^{\,i} + \frac{8\pi e^2}{Q^2} \sum_{k'} \frac{n(\vec{k}' - \vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} v_Q$$

which he writes as

$$v_Q = v_Q^{\,i} - v_Q \sum_{k'} A(\vec{k},\vec{k}')$$

solving for v_Q

$$v_Q = \frac{v_Q^{\,i}}{1 + \sum_{k'} A(\vec{k},\vec{k}')} \qquad (2.13)$$

or

$$v_Q = \frac{v_Q^{\,i}}{\varepsilon(Q)} \qquad (2.14)$$

where $\varepsilon(Q) = 1 + \sum_{k'} A(\vec{k},\vec{k}') = 1 + \frac{\beta f(u)}{2u^2}$ as before.

In eq.(2.14) $\varepsilon(Q)$ screens the bare-ion interaction to give the total matrix element.

6. Bailyn's Hartree Fock Result

The complication here introduced is that both the ions and the electrons are shielded by electron clouds, while in the Hartree approximation only the ions were considered as shielded. Bailyn extends Bardeen's method to take account of the exchange and correlation effects. He uses the Hartree-Fock equation and obtains a matrix element which is not independent of the initial electron wave-vector $\vec{k}$. His eq.(24) and (25) can be written

$$v_{Qk} = v_Q^{\,i} - 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{1}{|\vec{k} - \vec{k}'|^2} - \frac{1}{|\vec{k} + \vec{k}' - \vec{Q}|^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} v_{Qk'} \tag{2.15}$$

which he writes as $$v_{Qk} = v_Q^{\,i} - \sum_{k'} A(\vec{k},\vec{k}') v_{Qk'} \tag{2.16}$$

The first approximation made is that he assumes $v_{Qk'}$ to be independent of k', then eq.(2.16) becomes

$$v_{Qk} = v_Q^{\,i} - v_{Qk} \sum_{k'} A(\vec{k},\vec{k}') \tag{2.17}$$

Solving for v_{Qk} we obtain

$$v_{Qk} = \frac{v_Q^{\,i}}{1 + \sum_{k'} A(\vec{k},\vec{k}')} \tag{2.18}$$

$$= \frac{v_Q^{\,i}}{\varepsilon_{el}(Q)} \tag{2.19}$$

where $$\varepsilon_{el}(Q) = 1 + \sum_{k'} A(\vec{k},\vec{k}') \tag{2.20}$$

When exchange and correlation effects are included one must distinguish between the "proton-proton" and the "proton-electron" dielectric constant. We shall explain the difference further on. What Bailyn derives is the "proton-electron" dielectric constant,

which is the one to be used in conjunction with the scattering matrix element. We have used the symbol ε_{el} to denote it.

The second approximation made is that he averages $A(\vec{k},\vec{k}')$ over $\vec{k}$, then eq.(2.20) becomes

$$\varepsilon_{el}(Q) = 1 + \sum_{k'} \left\langle A(\vec{k},\vec{k}') \right\rangle_{avk} \qquad (2.21)$$

We now give the details for Bailyn's $\varepsilon_{el}(Q)$. Written out, eq.(2.20) is

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{1}{|\vec{k} - \vec{k}'|^2} - \frac{1}{|\vec{k} + \vec{k}' - \vec{Q}|^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (2.22)$$

The term $\frac{4}{Q^2}$ is the Coulomb term yielding the Hartree result, while the terms $\frac{1}{|\vec{k} - \vec{k}'|^2}$ and $\frac{1}{|\vec{k} + \vec{k}' - \vec{Q}|^2}$ are due to exchange effects. The singularity in $\frac{1}{|\vec{k} - \vec{k}'|^2}$ for $|\vec{k} - \vec{k}'| \to 0$ occurs because correlation has not yet been taken into account. Bohm and Pines (B53) assume that for all wavelengths larger than a certain cutoff the electrons move in a collective fashion and form a plasma (this is the so-called long range correlation). They neglect the influence of the plasma on the electron-ion interaction. If the Coulomb interaction is Fourier analyzed into two parts

$$\frac{e^2}{r} = 4\pi e^2 \left(\sum_{k'' < k_c} \frac{e^{i\vec{k}''\cdot\vec{r}}}{k''^2} + \sum_{k'' > k_c} \frac{e^{i\vec{k}''\cdot\vec{r}}}{k''^2} \right) \tag{2.23}$$

where $\vec{r} = \vec{r}_1 - \vec{r}_2$ then only the second part must be kept, i.e. all modes for which $k'' < k_c$ are thrown out and there remains the short range interaction H_{sr} which is analogous to the screened Coulomb potential $\frac{e^2}{r} \exp(-k_s r)$ of sec.1.

so
$$H_{sr}(r) = 4\pi e^2 \sum_{k'' > k_c} \frac{e^{i\vec{k}''\cdot\vec{r}}}{k''^2} \tag{2.24}$$

which we write

$$H_{sr}(r) = 4\pi e^2 \sum_{k''} \frac{e^{i\vec{k}''\cdot\vec{r}}}{\varepsilon' k''^2} \tag{2.25}$$

where

$$\varepsilon' = \begin{cases} \infty & \text{for } k'' < k_c \\ 1 & \text{for } k'' > k_c \end{cases} \tag{2.26}$$

We will now use this result to introduce correlation into eq.(2.22). All modes for which $|\vec{k} - \vec{k}'| < k_c$ (the plasma) must be removed. This is accomplished by writing $\frac{1}{\varepsilon' |\vec{k} - \vec{k}'|^2}$ instead of $\frac{1}{|\vec{k} - \vec{k}'|^2}$ in eq.(2.22) which becomes

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{1}{\varepsilon' |\vec{k} - \vec{k}'|^2} - \frac{1}{\varepsilon' |\vec{k} + \vec{k}' - \vec{Q}|^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{2.27}$$

Bailyn computes the volume averages $\left\langle \frac{1}{\varepsilon' |\vec{k} - \vec{k}'|^2} \right\rangle_{avk}$ and

$\left\langle \frac{1}{\varepsilon' |\vec{k} + \vec{k}' - \vec{Q}|^2} \right\rangle_{avk}$ over the sphere $|\vec{k}| = k_F$.

To do this he uses the transformation $\vec{k}'' = \vec{k}' - \vec{Q}$ for the second average, eq.(2.27) becomes

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{3h(x)}{k_F^2} - \frac{3h(x')}{k_F^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{2.28}$$

where

$$h(x) = \begin{cases} f(x) - x_o & \text{for } 0 < x < 1-x_o \\ \frac{1}{4} - \frac{x_o}{2} + \frac{1-x^2}{4x} \ln \frac{1+x}{x_o} + \frac{3x^2-1+x_o^2}{8x} & \text{for } 1-x_o < x < 1+x_o \\ f(x) & \text{for } 1+x_o < x < 3 \end{cases}$$

and $f(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right|$, $x = k'/k_F$, $x' = k''/k_F$, $x_o = k_c/k_F$.

We will work in the parabolic band approximation $E_{k'} = \frac{\hbar^2}{2m'} k'^2$ because it yields a simple expression which can easily be compared to Hone's work (H 60). The equations for $E_{k'} = \frac{\hbar^2 k_F^2}{2m'} (p'x^2 - p'q'x^4)$ will be given later on.

There are two integrals to evaluate (one for h(x) and one for h(x')). They can be combined into one and the final result is (see Appendix A for details).

$$\varepsilon_{el}(0) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u} \int_{y_o}^{1+2u} 3h(x) x Q(x,u) dx \qquad (2.29)$$

where $\beta = 2/\pi a_o k_F$; $\quad y_o = \begin{cases} 1 - 2u & \text{for } u < .5 \\ 0 & \text{for } u > .5 \end{cases}$

$$Q(x,u) = \begin{cases} \ln \left| \frac{x + u}{x - u} \right| & \text{for } x < |2u - 1| \\ \ln \left| \frac{4u(x \pm u)}{1 - x^2} \right| \quad \text{with} \begin{cases} + \text{ for } x < 1 \\ - \text{ for } x > 1 \end{cases} & \text{for } x > |2u - 1| \end{cases}$$

7. Hone's Extension of Bardeen-Pines' Result

We know that the electrons tend to follow the motion of the ions with the result that the ions are screened. This is described by the total dielectric constant. The correlation effects screen the

electrons and this will be described by the dielectric constant $\varepsilon' = 1 + k_s^2/k''^2$. Hone extends the Bardeen-Pines (B55) procedure to obtain the integral equation for the matrix element

$$v_{Qk} = v_Q^i + 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{|\vec{k} - \vec{k}'|^2} \right) \frac{n(\vec{k}' - \vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} v_{Qk'} \qquad (2.30)$$

Correlation has not yet been taken into account, so again we get the singularity in $\frac{1}{|\vec{k} - \vec{k}'|^2}$. As mentioned, Hone describes correlation as electron-electron screening using the dielectric constant

$$\varepsilon' = 1 + k_s^2/|\vec{k} - \vec{k}'|^2 \qquad (2.31)$$

whereas Bailyn used

$$\varepsilon' = \begin{cases} \infty & \text{for } |\vec{k} - \vec{k}'| < k_c \\ 1 & \text{for } |\vec{k} - \vec{k}'| > k_c \end{cases} \qquad (2.32)$$

Eq.(2.30) thus yields

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{\varepsilon'|\vec{k} - \vec{k}'|^2} \right) \frac{n(\vec{k}' - \vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (2.33)$$

Hone applies a first transformation to the term multiplying $n(\vec{k}' - \vec{Q})$ in equation (2.33), which is

$$\vec{k}' - \vec{Q} \rightarrow -\vec{k}' \qquad (2.34)$$

Using eq.(2.34) and substituting for ε' he gets

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{1}{|\vec{k} - \vec{k}'|^2 + k_s^2} - \frac{1}{|\vec{k} + \vec{k}' - \vec{Q}|^2 + k_s^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{2.35}$$

He then computes the surface averages $\left\langle \frac{1}{|\vec{k} - \vec{k}'|^2 + k_s^2} \right\rangle_{avk}$ and

$\left\langle \frac{1}{|\vec{k} + \vec{k}' - \vec{Q}|^2 + k_s^2} \right\rangle_{avk}$ over the sphere $|\vec{k}| = k_F$ and eq.(2.35) becomes

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{T(x)}{k_F^2} - \frac{T(x')}{k_F^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{2.36}$$

where $T(x) = \frac{1}{4x} \ln \left| \frac{(1 + x)^2 + x_o^2}{(1 - x)^2 + x_o^2} \right|$, $x = k'/k_F$, $x_o = k_s/k_F$.

To perform the integration over $\vec{k}'$ Hone applies a second transformation to the energy denominator multiplying the term $T(x')$ of eq.(2.36)

$$\vec{k}'' = \vec{k}' - \vec{Q} \tag{2.37}$$

Then Hone makes a mistake in the limits of integration (in the determination of the expression for Θ_c the lower limit of integration for Θ, see Appendix B for details). So here we will not follow Hone but rather proceed as follows.

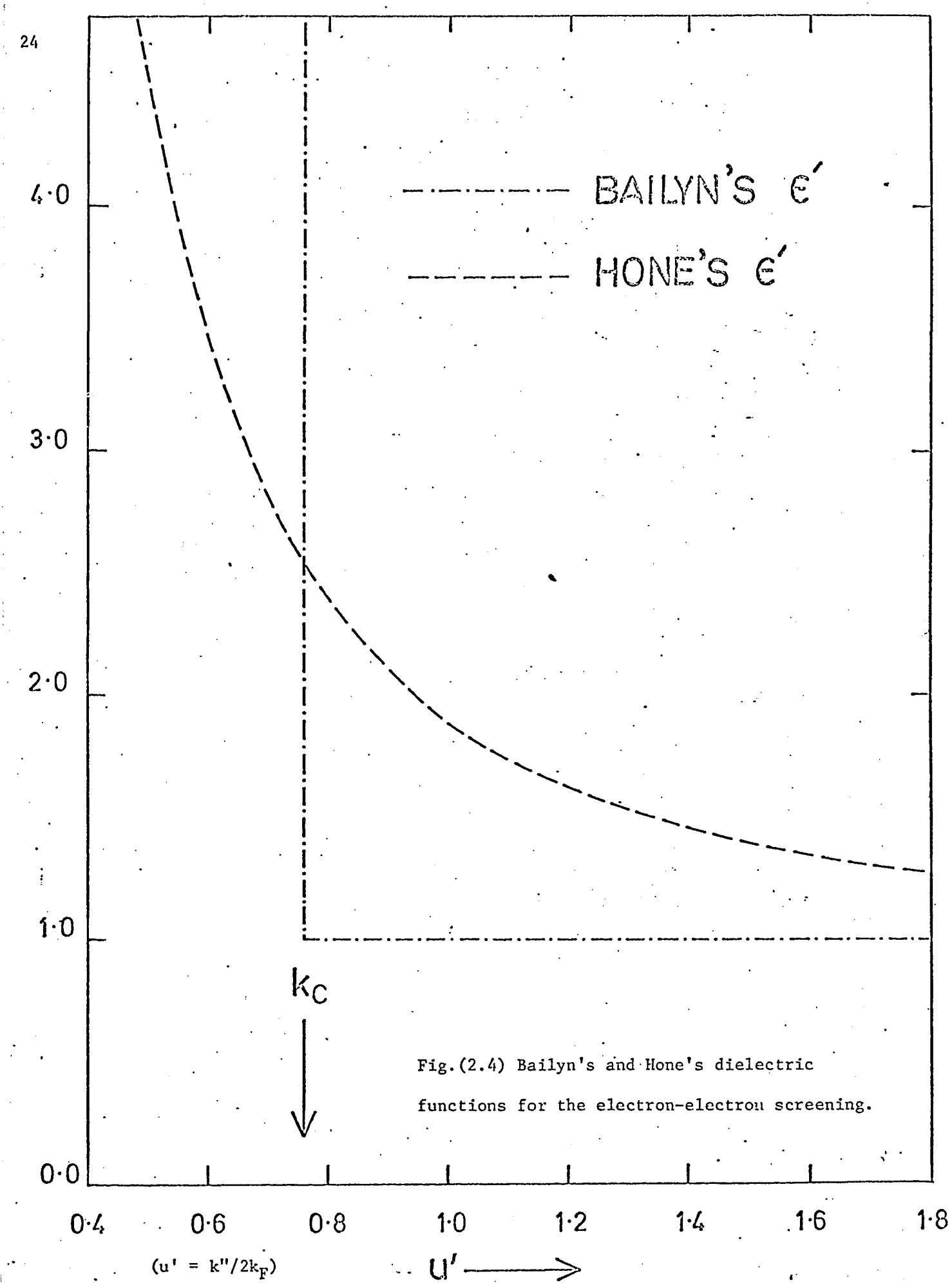


Fig.(2.4) Bailyn's and Hone's dielectric functions for the electron-electron screening.

The expression we are trying to integrate (eq.(2.36)) is analogous to that of Bailyn, the only difference being that $T(x)$ replaces $3h(x)$. Further, the notation brings out more similarities, for example Bailyn's transformation $\vec{k}'' = \vec{k}' - \vec{Q}$ is identical to that of Hone (eq.(2.37)). So we proceed the same way as we did for Bailyn's expression in Appendix A and obtain

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u}\int_{y_o}^{1+2u} T(x)xQ(x,u)dx \qquad (2.38)$$

where y_o and $Q(x,u)$ are defined as in equation (2.29) chapter 2 sec.5.

8. Recapitulation and Simplification of the Procedure of Bailyn and Hone

The essential equation for $\varepsilon_{el}(Q)$ is

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'}\left(\frac{2}{Q^2} - \frac{1}{\varepsilon'|\vec{k} - \vec{k}'|^2}\right)\frac{n(\vec{k}' - \vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (2.39)$$

where
$$\varepsilon' = \begin{cases} \infty & \text{for } |\vec{k} - \vec{k}'| < k_c \\ 1 & \text{for } |\vec{k} - \vec{k}'| > k_c \end{cases} \qquad \text{Bailyn}$$

and
$$\varepsilon' = 1 + k_s^2/|\vec{k} - \vec{k}'|^2 \qquad \text{Hone}$$

The difference between these two expressions for ε' is depicted in fig.(2.4) where they are plotted as functions of $k'' = |\vec{k} - \vec{k}'|$.

Now we discuss equation(2.39). As mentioned the term $\frac{2}{Q^2}$ yields the Hartree result. The term $\frac{1}{|\vec{k} - \vec{k}'|^2}$ arises from exchange

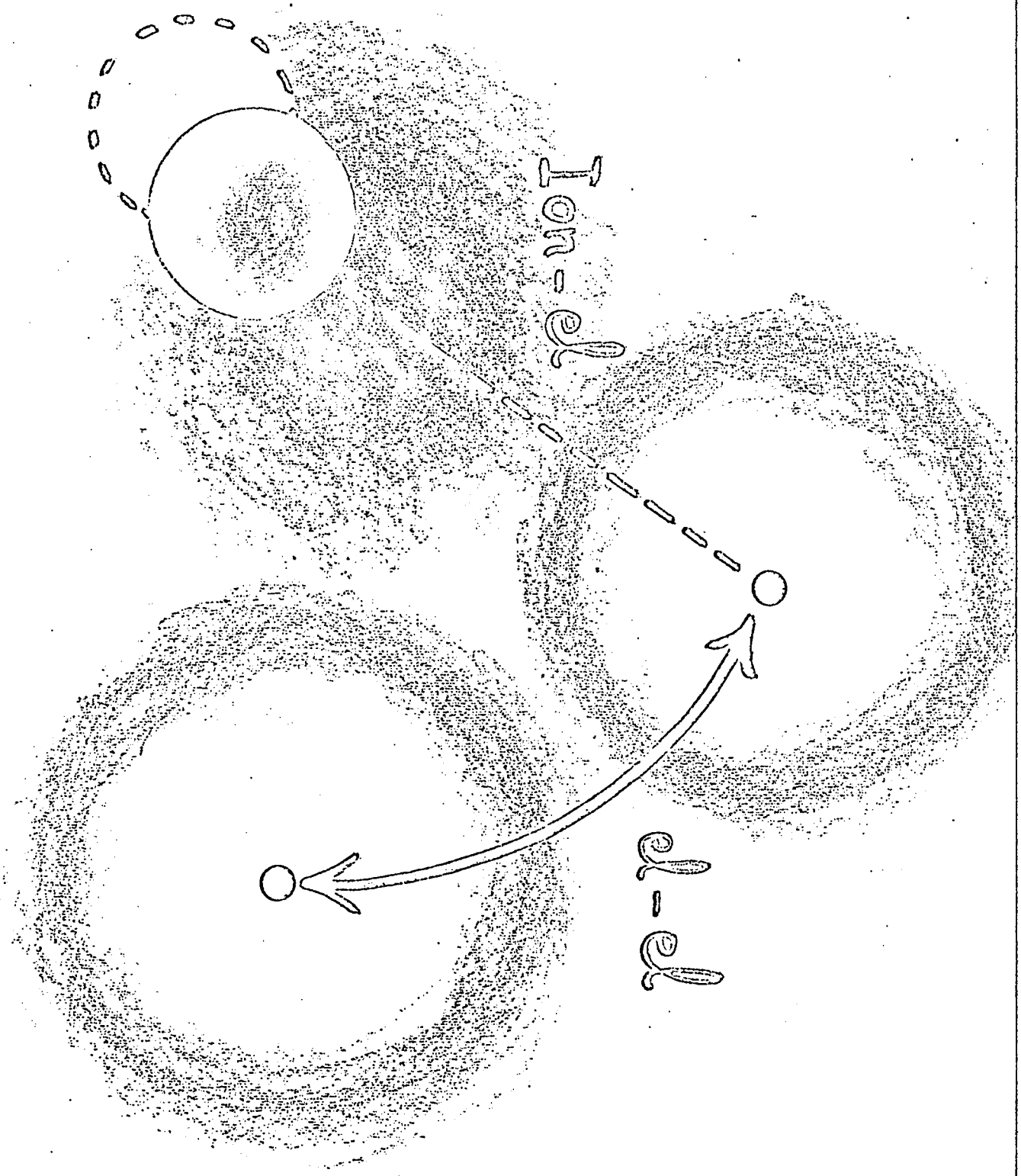


Fig. (2.5) The ion-electron and electron-electron screening.

effects and ε' describes the shielding of electrons by one another, i.e. the ionic potential is not the only thing shielded, but the electrons also shield one another. Thus while we are trying to derive a dielectric constant $\varepsilon_{el}(Q)$ to describe the shielding of an ion, we need another dielectric function ε' to describe the electron-electron shielding. This situation is depicted in fig.(2.5). Hone chose the function $\varepsilon' = 1 + k_s^2/k''^2$ (which is nothing else but the long wavelength approximation of the Hartree result) because it was simple enough to enable him to carry out the integration over $\vec{k}$ (involved in the averaging process) and the integration over $\vec{k}'$.

Before going any further we will simplify the treatment given to eq.(2.39). We will show that the transformations

$$\vec{k}' - \vec{Q} \rightarrow -\vec{k}' \qquad (2.40a)$$

and

$$\vec{k}' - \vec{Q} = \vec{k}'' \qquad (2.40b)$$

made by Hone are unnecessary. The first transformation was made to eliminate the term $n(\vec{k}' - \vec{Q})$ in eq.(2.39) and gave rise to the term $\dfrac{1}{\varepsilon'|\vec{k} + \vec{k}' - \vec{Q}|^2}$ in eq.(2.35). Then the second transformation was applied to evaluate the integral over $\vec{k}'$ for the term obtained through the average $\left\langle \dfrac{1}{\varepsilon'|\vec{k} + \vec{k}' - \vec{Q}|^2} \right\rangle_{avk}$.

We now show that these transformations cancel each other. We write eqs.(2.40a) and (2.40b) as

$$\vec{k}' - \vec{Q} = -\vec{k}'_{New} \tag{2.41}$$

and $$\vec{k}'_{New} - \vec{Q} = \vec{k}'' \tag{2.42}$$

Substituting $\vec{k}'_{New}$ as given by eq.(2.42) into eq.(2.41) we get

$$\vec{k}' - \vec{Q} = -(\vec{Q} + \vec{k}'')$$

which yields when simplified

$$\vec{k}' = -\vec{k}'' \tag{2.43}$$

Eq.(2.43) shows that these two transformations are "circular" i.e. we end up at essentially the same point where we started. So we proceed to integrate eq.(2.39) as it stands. First we take the average over $\vec{k}$ to get

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{AV(x)}{k_F^2} \right) \frac{n(\vec{k}' - \vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{2.44}$$

where $AV(x) = 3h(x)$ in the case of Bailyn,

and $AV(x) = T(x)$ in the case of Hone.

We then proceed to integrate eq.(2.44) without making any transformations. The details are given in Appendix C, the result is

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u} \int_{y_o}^{1+2u} AV(x) x Q(x,u) dx \tag{2.45}$$

where β, y_o, $Q(x,u)$ are defined as before.

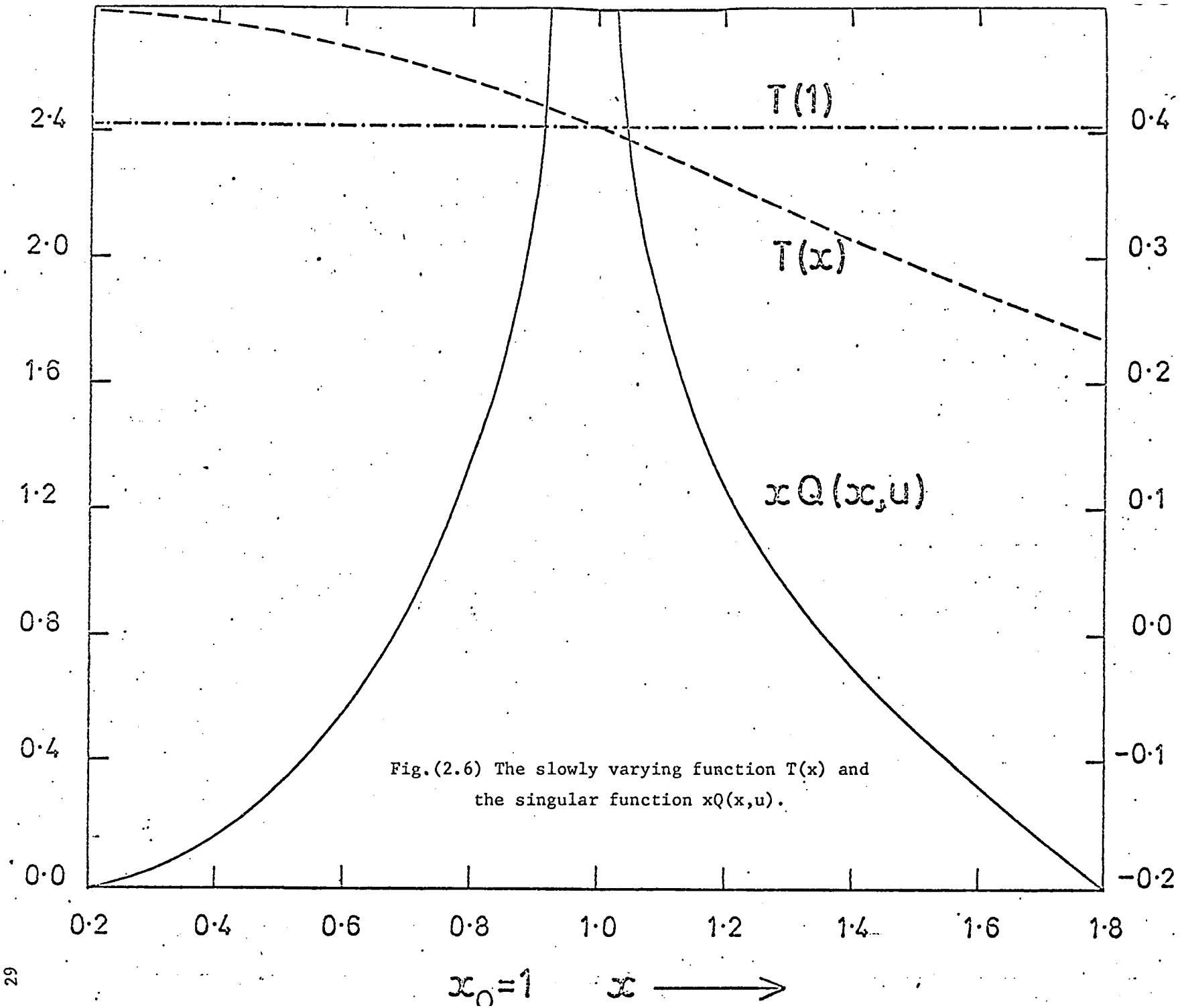


Fig.(2.6) The slowly varying function T(x) and the singular function xQ(x,u).

9. The Procedure of Factorizing out the Slowly Varying Part

We will now discuss a procedure which will be of general usefulness in subsequent derivations. We will use the ε_{el} derived from Hone's approach. Like the other equations for ε_{el} eq.(2.37) can be conveniently written in the form

$$\varepsilon_{el} = 1 + \chi + E \tag{2.46}$$

where

$$\chi = \frac{\beta f(u)}{2u^2} \tag{2.47}$$

and

$$E = -\frac{\beta}{4u}\int_{y_o}^{1+2u} T(x)\,xQ(x,u)\,dx \tag{2.48}$$

The part $1 + \chi$ gives the Hartree contribution, while E is the exchange and correlation term (which we will call the EC term for short). We can perform the integration numerically to evaluate the EC term. Alternatively we can proceed as follows. We note that the integrand consists of two functions: $T(x)$, which is a slowly varying function of x and $xQ(x,u)$ which is quite rapid and has a singularity at $x = 1$ (see fig.(2.6)). So we factorize out the slowly varying $T(x)$ at the point $x = 1$ (the singular point of $Q(x,u)$). This amounts to taking $T(x)$ as constant and we see from fig.(2.6) that the error made on one side of the singularity tends to balance the error made on the other side. At any rate, most of the contribution to the integral comes from the neighbourhood of the singularity. This is why we factorize $T(x)$ at

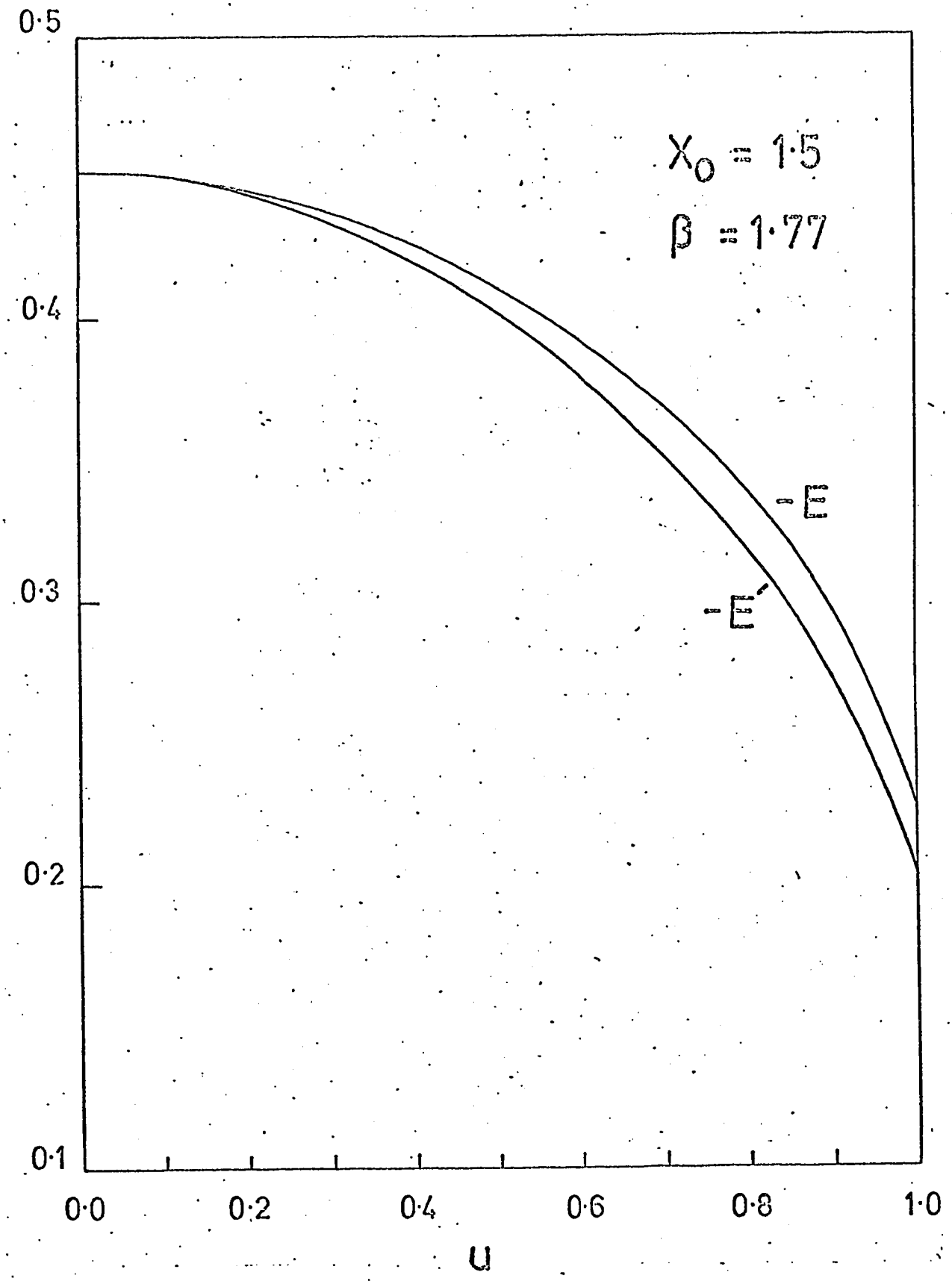


Fig.(2.7) The exchange and correlation terms E and E'.
(actually -E and -E' are plotted)

$x = 1$. The EC term then becomes

$$E' = -\beta T(1) f(u) \tag{2.49}$$

where $$T(1) = \frac{1}{4} \ell n \left| \frac{4 + x_o^2}{x_o^2} \right|$$

and we have used the result

$$\int_{y_o}^{1+2u} xQ(x,u)dx = 4uf(u) \tag{2.50}$$

In fig.(2.7) we have plotted the EC terms E and E' as given by eq.(2.48) and eq.(2.49) respectively. We see that E' is very close to E and $E' \to E$ for $Q \to 0$. It was found empirically that $E'' = -\beta T(1 + u^2/4) f(u)$ reproduces E almost exactly.

The idea of factorizing out the slowly varying part will be used later on (in a different context). We have given the details here to throw light on the procedure by showing that it gives a result which is not very different from the complete integral.

We may note here that similar procedures have been used in other fields of physics, e.g., in the evaluation of the electronic specific heat (S40) and in the calculation of the impurity scattering in semiconductors (S61).

We should also note that a very similar approximation was made earlier in the derivation of ε_{el}. Namely in chap.1 sec.6 $v_{Qk'}$ was assumed to be a slowly varying function of k' and was factorized out

of the integral to obtain eq.(2.17). It should also be pointed out that other approximations have been made (for example the averaging over k) and our approximation is merely one more approximation, whose validity we have justified.

10. Comparison of the Bailyn and Hone Screening Method for the Electron-Electron Interaction

We saw that Bailyn and Hone describe correlation through screening, i.e. electron-electron correlation is described by means of the dielectric constant ε'.

$$\text{Bailyn used} \quad \varepsilon' = \begin{cases} \infty & \text{for } k'' < k_c \\ 1 & \text{for } k'' > k_c \end{cases}$$

$$\text{Hone used} \quad \varepsilon' = 1 + k_s^2/k''^2$$

Even though k_s and k_c come from different concepts, we shall put $k_s = k_c$ for the purpose of our discussion. We will examine the differences between the screened potentials obtained using these two dielectric constants. The Fourier transform of the Coulomb potential is $\frac{4\pi e^2}{k''^2}$ * and that of the screened potential is $\frac{4\pi e^2}{\varepsilon' k''^2}$ so we have:

$$\text{for the unscreened potential} \quad 4\pi e^2 \sum_{k''^2} \frac{e^{i\vec{k}''\cdot\vec{r}}}{k''^2} = \frac{e^2}{r} \qquad (2.51)$$

* for the electron gas in a container of unit volume

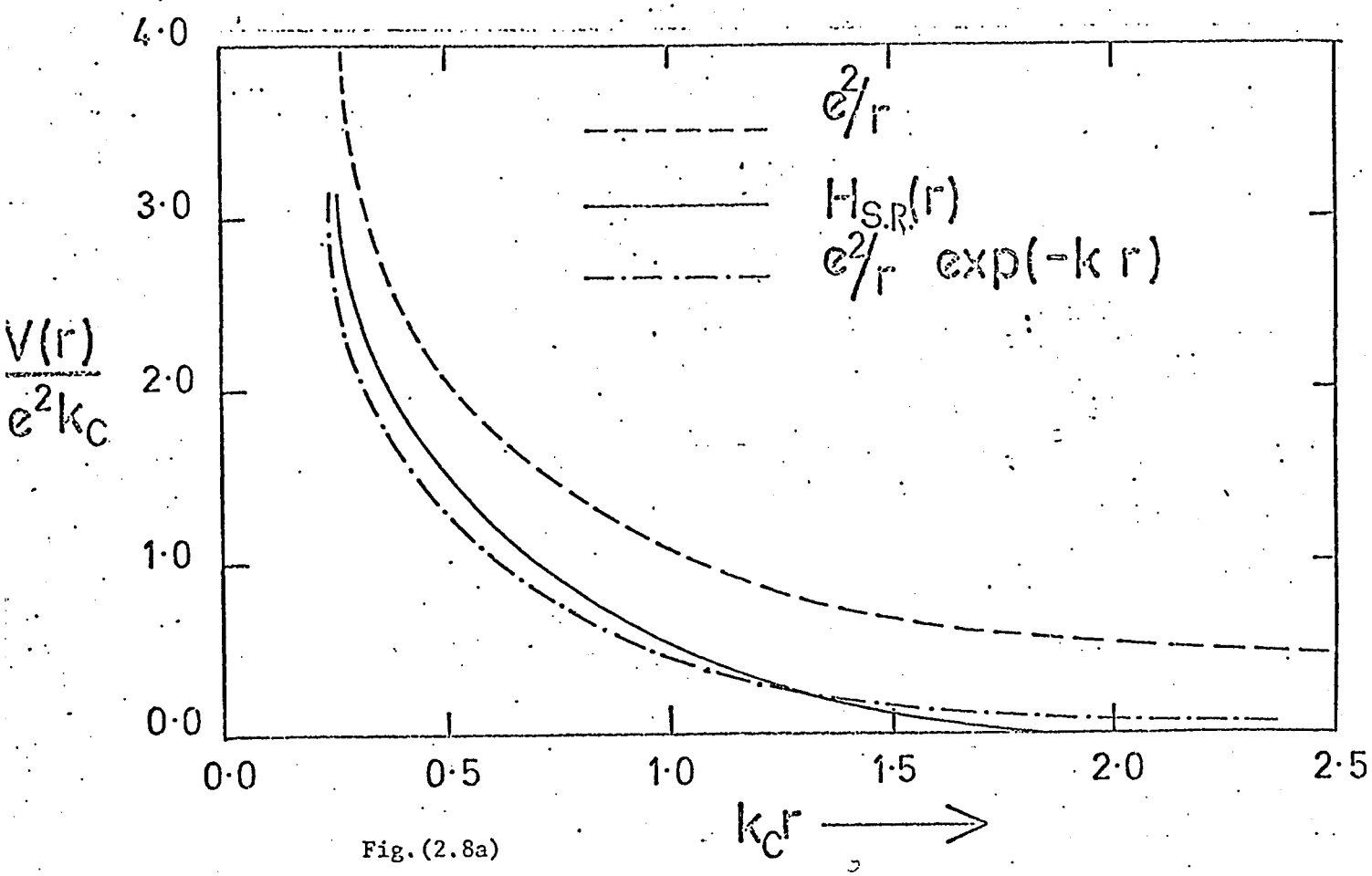


Fig.(2.8a)

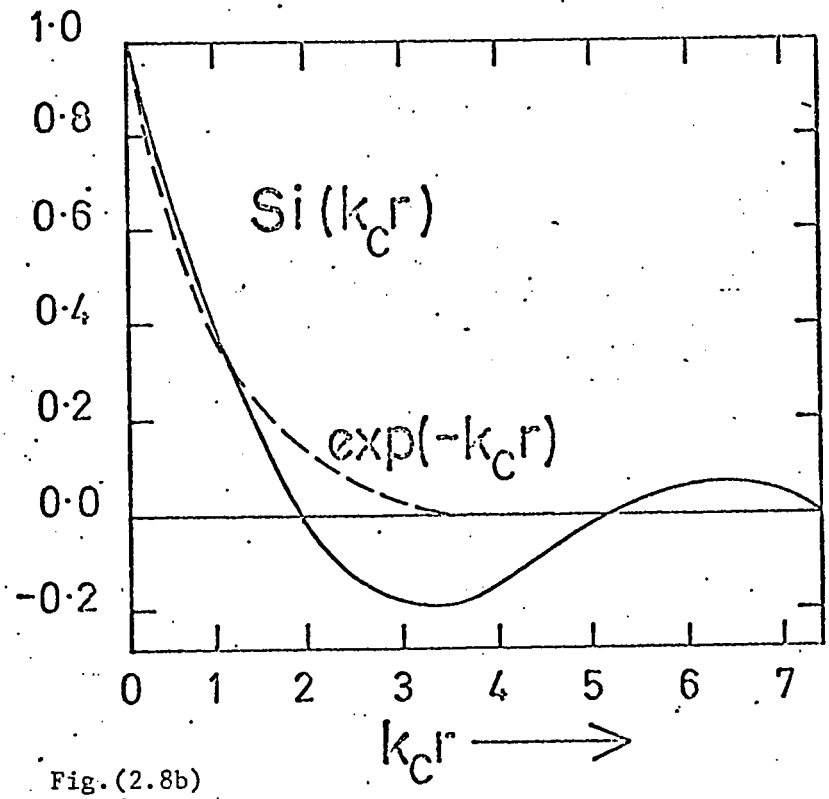


Fig.(2.8b)

for Bailyn's ε' $$4\pi e^2 \sum_{k''>k_c} \frac{e^{i\vec{k}''\cdot\vec{r}}}{k''^2} = \frac{e^2}{r} \mathrm{Si}(k_c r) \qquad (2.52)$$

for Hone's ε' $$4\pi e^2 \sum_{k''} \frac{e^{i\vec{k}''\cdot\vec{r}}}{k''^2 + k_c^2} = \frac{e^2}{r} \exp(-k_c r) \qquad (2.53)$$

where $$\mathrm{Si}(y) = 1 - \frac{2}{\pi}\int_0^y \frac{\sin x}{x}\, dx$$

The screened potentials of eqs.(2.52) and (2.53) are plotted (together with the Coulomb potential) in fig.(2.8a) (P63). We see that the Bailyn and Hone results are similar. Finer differences are brought out in fig.(2.8b) where $\exp(-k_c r)$ and $\mathrm{Si}(k_c r)$ are plotted (R61). The oscillations in $\mathrm{Si}(k_c r)$ are due to the sharp cutoff at wave vector k_c (see fig.(2.4)).

Since the Bailyn and the Hone screened potentials are similar, we would expect that the exchange and correlation term E obtained by both methods should be of comparable magnitude. Let us investigate this. We have found for this exchange term

$$E = -\frac{\beta}{4u}\int_{y_o}^{1+2u} AV(x)\,x\,Q(x,u)\,dx \qquad (2.54)$$

where $AV(x) = 3h(x)$ (derived from Bailyn's work)

or $AV(x) = T(x)$ (derived from Hone's work)

So by the previous reasoning the functions T(x) and 3h(x) should be comparable (when $k_s = k_c$). They are plotted in fig.(2.9)

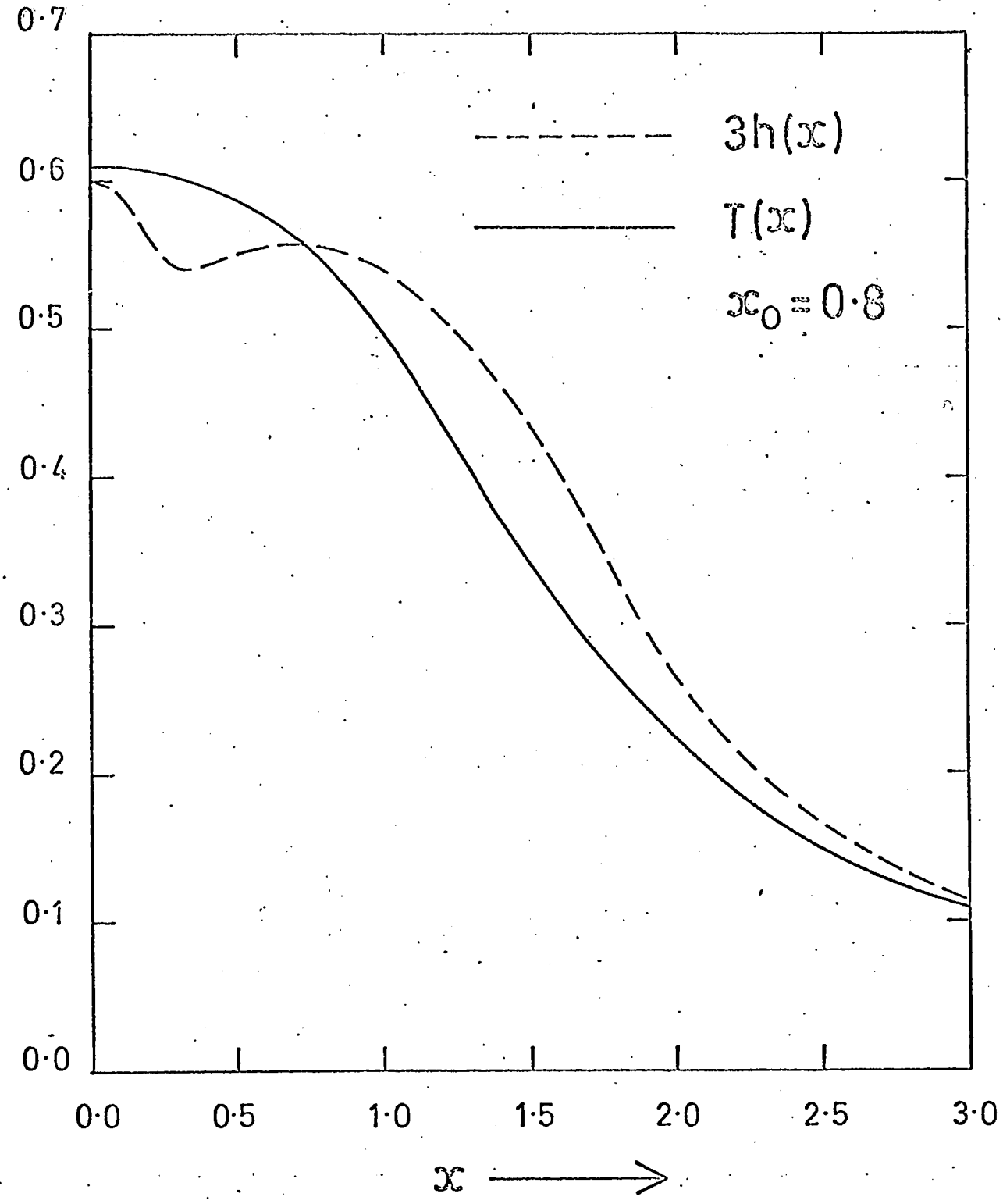


Fig.(2.9) The function 3h(x) from Bailyn's work and T(x) from Hone's work.

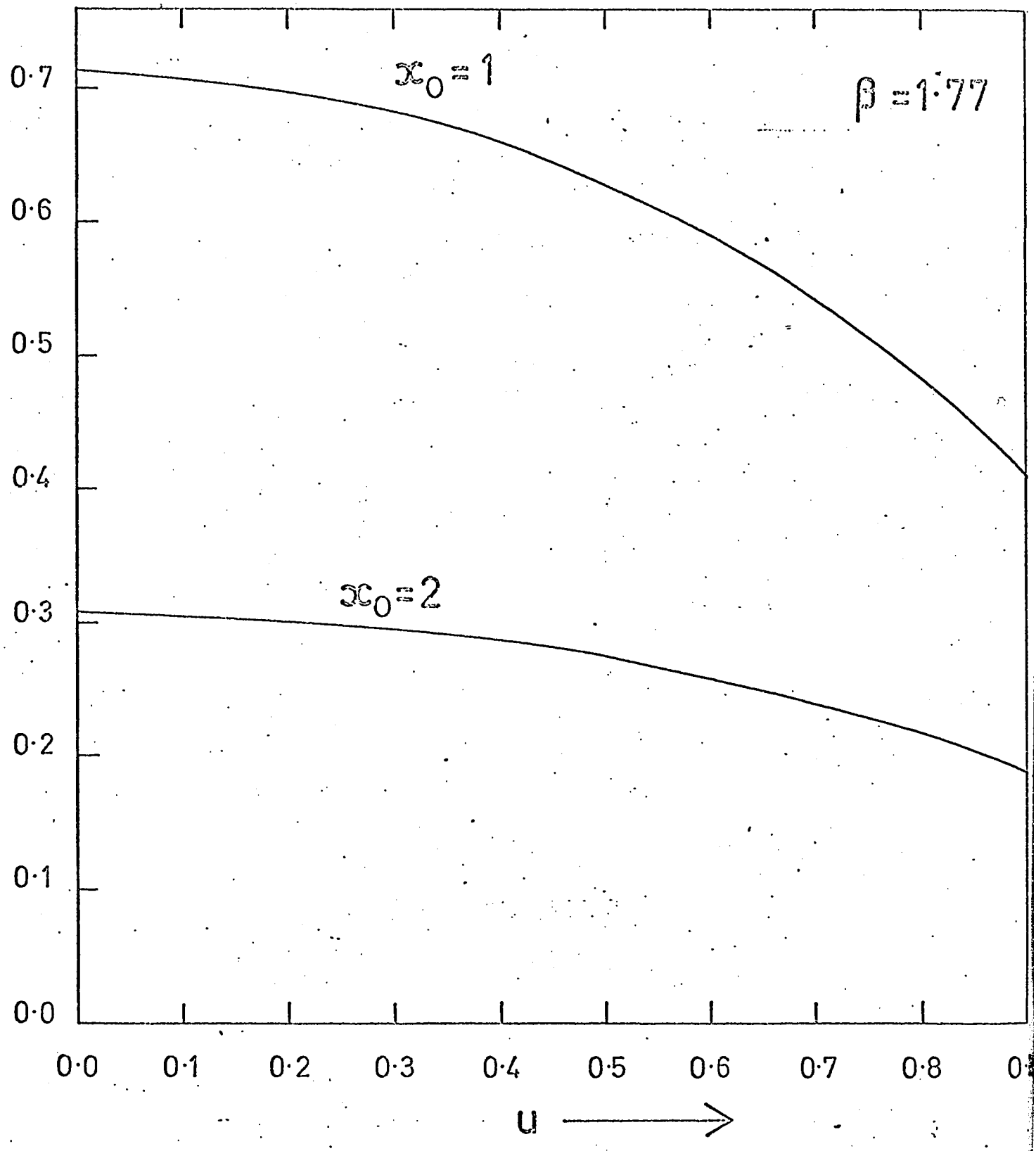


Fig.(2.10) The exchange and correlation term, derived from Hone's work, for $k_s = k_F$ and $k_s = 2k_F$. (-E is plotted)

We find that they are indeed similar.

The choice of the screening parameter k_s (or k_c) is very important since the variation of the EC term with k_s is quite drastic (much more than the small differences between T(x) and 3h(x)). To show this we choose AV(x) = T(x) and plot -E for $k_s = k_F$ and $k_s = 2k_F$ in fig. (2.10).

11. Darby's Treatment of Hone's Result

Darby's starting point (D64) is the equation

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{1}{|\vec{k}-\vec{k}'|^2+k_s^2} - \frac{1}{|\vec{k}+\vec{k}'-\vec{Q}|^2+k_s^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}}$$

To obtain an analytical expression he proceeds as follows: choosing the z axis along $\vec{k}$ he writes out

$$\frac{1}{|\vec{k} - \vec{k}'|^2 + k_s^2} = \frac{1}{k^2 + k'^2 + k_s^2 - 2kk'\cos\Theta}$$

where Θ is the angle between $\vec{k}$ and $\vec{k}'$. He then sets $\mu = \cos\Theta$ and expands the right hand side in Legendre polynomials (of argument cos Θ)

$$\frac{1}{k^2 + k'^2 + k_s^2 - 2kk'\mu} = \sum_{\ell=o}^{\infty} f_\ell P_\ell(\mu) \qquad (2.55)$$

For example the zeroth term is (using the formula for the coefficient

f_ℓ given in Appendix D)

$$f_o = \frac{1}{2}\int_{-1}^{+1} \frac{d\mu}{k^2 + k'^2 + k_s^2 - 2kk'\mu} \qquad (2.56)$$

$$= \frac{1}{2b} \ell n\left|\frac{a + b}{a - b}\right|$$

where $a = k^2 + k'^2 + k_s^2$ and $b = 2kk'$

Darby retains only the zeroth term (the others being much smaller) and thus obtains

$$\frac{1}{|\vec{k} - \vec{k}'|^2 + k_s^2} \approx \frac{1}{2b} \ell n\left|\frac{a + b}{a - b}\right| \qquad (2.57)$$

For the second expression $\frac{1}{|\vec{k} + \vec{k}' - \vec{Q}|^2 + k_s^2}$ he defines $\vec{r} = \vec{k} - \vec{Q}$ and expands using $\mu' = \cos\Theta'$ where Θ' is the angle between $\vec{r}$ and $\vec{k}'$. He gets

$$\frac{1}{|\vec{k}' + \vec{r}|^2 + k_s^2} \approx \frac{1}{2B} \ell n\left|\frac{A + B}{A - B}\right| \qquad (2.58)$$

where $A = k'^2 + r^2 + k_s^2$ and $B = -2rk'$

We obtain identical results by averaging over k and r instead of doing an expansion in Legendre polynomials and retaining the zeroth term i.e.

$$\left\langle \frac{1}{|\vec{k} - \vec{k}'|^2 + k_s^2} \right\rangle_{avk} = \frac{1}{2b} \ln \left| \frac{a + b}{a - b} \right| \qquad (2.59)$$

$$\left\langle \frac{1}{|\vec{k}' + \vec{r}|^2 + k_s^2} \right\rangle_{avr} = \frac{1}{2B} \ln \left| \frac{A + B}{A - B} \right| \qquad (2.60)$$

See appendix D for a proof.

Using eqs. (2.57) and (2.58) we can write the final result

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u} \int_0^1 AV(x) x \ln g_o \, dx \qquad (2.61)$$

where $AV(x) = \frac{1}{2b} \ln \left| \frac{a + b}{a - b} \right| + \frac{1}{2B} \ln \left| \frac{A + B}{A - B} \right|$ and $g_o = \left| \frac{x + u}{x - u} \right|$

This result is somewhat similar to those previously obtained. We note one difference: the angular dependence in $r = |\vec{k} - \vec{Q}|$ has not been eliminated and Darby had to take some average for the angle between $\vec{k}$ and $\vec{Q}$.

CHAPTER III

Derivation of Various Expressions for the Dielectric Function

Apart from Bailyn's and Hone's work various expressions for the exchange and correlation term have been derived to various degrees of approximation by several authors. Amongst these are: Toya (T58), Hubbard (H57) (who modified his expression, which was later used by Sham (S65b), Heine-Abarenkov (H64), Ho et al (H67), Schneider and Stoll (S66, S66a)), Geldart-Vosko (G65), Kleinman (K67) and recently Takahashi (T68). These authors used different techniques than Bailyn and Hone. Notwithstanding this we will show that the results of the above mentioned authors can be obtained in a straightforward way from the basic equations of Bailyn and Hone. We then continue to show that electron-electron screening can be described more accurately, and using the factorization procedure introduced in chapter II, we obtain new expressions for the exchange and correlation term.

Recently Geldart and Taylor (G69) have proposed a new screening function. However, their results are given in the form of a numerical table and we shall not discuss them further here.

1. Derivation of Hubbard's Expression

Our starting point is the equation

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{|\vec{k}-\vec{k}'|^2 + k_s^2} \right) \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (3.1)$$

We apply the transformation $\vec{k}'-\vec{Q} \to -\vec{k}'$ and obtain

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{|\vec{k}+\vec{k}'-\vec{Q}|^2 + k_s^2} \right) \frac{n(-\vec{k}') - n(-\vec{k}'+\vec{Q})}{E_{-k'} - E_{-k'+Q}}$$

We make use of the approximation introduced by Hubbard

$$|\vec{k} - \vec{k}' + \vec{Q}|_{av} \approx k_F^2 + Q^2 \qquad (3.2)$$

(where the subscript av denotes average values). Further we have

$$|\vec{k} + (\vec{k}' - \vec{Q})|^2_{avk} = |\vec{k} - (\vec{k}' - \vec{Q})|_{avk}$$

when averages are taken over the sphere $|\vec{k}| = k$. Then using eq.(3.2)

$$|\vec{k} + (\vec{k}' - \vec{Q})|^2_{av} \approx k_F^2 + Q^2 \qquad (3.3)$$

Using approximations (3.3) and also the properties $n(-\vec{k}') = n(\vec{k}')$, $E_{-k'} = E_{k'}$, etc., we obtain

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \left(\frac{2}{Q^2} - \frac{1}{Q^2 + k_F^2 + k_s^2} \right) \sum_{k'} \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}}$$

$$= 1 + \left[1 - \frac{1}{2} \frac{Q^2}{Q^2 + k_F^2 + k_s^2} \right] \chi(Q) \qquad (3.4)$$

where $\chi(Q) = \beta f(u)/2u^2$, $u = Q/2k_F$.

Eq.(3.4) is identical to Hubbard's improved equation as used by Sham (S65b), Heine-Abarenkov (H64) and Ho et al (H67).

2. Derivation of Kleinman's (K67) Expression

Our starting point (B67a) is the equation

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{1}{|\vec{k}-\vec{k}'|^2 + k_s^2} - \frac{1}{|\vec{k}+\vec{k}'-\vec{Q}|^2 + k_s^2} \right) \frac{n(k')}{E_{k'-Q} - E_{k'}} \qquad (3.5)$$

We make use of the approximation introduced by Hubbard

$$|\vec{k} - \vec{k}'|^2_{av} \approx k_F^2 \qquad (3.6)$$

and the approximation introduced in the last section

$$|\vec{k} + \vec{k}' - \vec{Q}|^2_{av} \approx k_F^2 + Q^2$$

Using these two approximations we get

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \left(\frac{4}{Q^2} - \frac{1}{k_F^2 + k_s^2} - \frac{1}{Q^2 + k_F^2 + k_s^2} \right) \sum_{k'} \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}}$$

$$= 1 + \left\{ 1 - \frac{1}{4} \left[\frac{Q^2}{k_F^2 + k_s^2} + \frac{Q^2}{Q^2 + k_F^2 + k_s^2} \right] \right\} \chi(Q) \qquad (3.7)$$

where $\chi(Q)$ is defined as in eq.(3.4). Eq.(3.7) is identical to that of Kleinman (K67).

3. Derivation of Toya's (T58) Expression

We start with

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{|\vec{k}-\vec{k}'|^2} \right) \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{3.8}$$

We do not introduce electron-electron screening but we use the Hubbard approximation

$$|\vec{k} - \vec{k}'|^2_{av} \approx k_F^2$$

and substitute into eq.(3.8) which we write in the form

$$\varepsilon_{el}(Q) = 1 + \left[1 - \frac{4}{8} \frac{1}{k_F^2} \right] \chi(Q) \tag{3.9}$$

Eq.(3.9) differs from Toya's only in that the factor $\frac{4}{8}$ is equal to $\frac{3}{8}$ in Toya's case, but this is irrelevant, since he replaces $\frac{3}{8}$ by $\frac{B}{4}$ and chooses $B = 1.21$ (T58).

4. Derivation of the Geldart-Vosko (G65, V65) Expression

We start with

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{|\vec{k}-\vec{k}'|^2 + k_s^2} \right) \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{3.10}$$

We note that the term $\frac{1}{|\vec{k}-\vec{k}'|^2 + k_s^2}$ is slowly varying as compared to the

singular energy term $\frac{1}{E_{k'-Q} - E_{k'}}$. (This is analogous to the factorization procedure of chapter II sect.9. In fig.(2.6) we plotted the functions T(x) and xQ(x,u). T(x) is the average of $\frac{1}{|\vec{k}-\vec{k}'|^2 + k_s^2}$ over $\vec{k}$ and xQ(x,u) results from the integration of $\frac{1}{E_{k'-Q} - E_{k'}}$ over the angular variables.

It was clearly shown that T(x) is slowly varying and could be factorized out of the integral). So factorizing out $\frac{1}{|\vec{k}-\vec{k}'|^2 + k_s^2}$ in eq.(3.10) we obtain

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \left(\frac{2}{Q^2} - \frac{1}{Q^2 + k_s^2} \right) \sum_{k'} \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}}$$

$$= 1 + \left[1 - \frac{1}{2} \frac{Q^2}{Q^2 + \xi k_F^2} \right] \chi(Q) \qquad (3.12)$$

where we have written $k_s^2 = \xi k_F^2$. Eq.(3.12) is identical to that of Geldart and Vosko (G65, V65).

5. Derivation of New Expressions

We start with

$$\varepsilon_{el} = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{|\vec{k}-\vec{k}'|^2} \right) \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (3.13)$$

We saw that the exchange term $\frac{1}{|\vec{k}-\vec{k}'|^2}$ must be screened to des-

cribe correlation. Hone used the dielectric function $\varepsilon' = 1+k_s^2/|\vec{k}-\vec{k}'|^2$ and thus the exchange term was changed to $\frac{1}{\varepsilon'|\vec{k}-\vec{k}'|^2}$. This simple expression for ε' was chosen to enable him to carry out the averaging over $\vec{k}$ and the integration over $\vec{k}'$. We will proceed in a different way. Instead of using this ε' to describe correlation, we will use the accurate dielectric function ε_{el}. This will make the treatment of the equation more difficult and we will recourse to our factorization process to solve it. The exchange term becomes $\frac{1}{\varepsilon_{el}|\vec{k}-\vec{k}'|^2}$ and eq.(3.13) can be written as

$$\varepsilon_{el} = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{\varepsilon_{el}|\vec{k}-\vec{k}'|^2} \right) \frac{n(\vec{k}'-\vec{Q})-n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (3.14)$$

We see that eq.(3.14) must be solved self-consistently i.e. the quantity we are trying to calculate (ε_{el}) appears inside the integral, so we must first calculate an approximate value for ε_{el}, substitute the result in the right hand side, recalculate ε_{el}, resubstitute and so on. We will proceed as follows. We first note that $\frac{1}{\varepsilon_{el}|\vec{k}-\vec{k}'|^2}$ is slowly varying as compared to the singular term $\frac{1}{E_{k'-Q} - E_{k'}}$. Factorizing out the slowly varying part, eq.(3.14) becomes

$$\varepsilon_{el} = 1 - 4\pi e^2 \left(\frac{2}{Q^2} - \frac{1}{\varepsilon_{el}\, Q^2} \right) \sum_{k'} \frac{n(\vec{k}'-\vec{Q})-n(\vec{k}')}{E_{k'-Q} - E_{k'}}$$

$$= 1 + \left[1 - \frac{1}{2\varepsilon_{el}} \right] \chi(Q) \qquad (3.15)$$

To a first approximation eq.(3.15) gives

$$\varepsilon_{el} = 1 + \chi(Q) \tag{3.16}$$

Substituting back into the right hand side of eq.(3.15) we get

$$\varepsilon_{el} = 1 + \left[1 - \frac{1}{2}\frac{1}{1 + \chi(Q)}\right]\chi(Q) \tag{3.17}$$

This is a new expression for ε_{el}. The Geldart--Vosko expression appears as an approximation to this equation when we take the long wavelength limit for the denominator of the term $\frac{1}{1 + \chi(Q)}$ i.e.

$$1 + \chi(Q) \approx 1 + k_s^2/Q^2 \tag{3.18}$$

Substituting back into eq.(3.17) we get

$$\varepsilon_{el} = 1 + \left[1 - \frac{1}{2}\frac{1}{1+k_s^2/Q^2}\right]\chi(Q) \tag{3.19}$$

which is the Geldart-Vosko equation (eq.(3.12)), written in a slightly different way.

We have thus found an interesting expression for ε_{el}. This expression (given by eq.(3.17)) is an approximation to the solution of eq.(3.15) which we obtain as follows. Multiply both sides by ε_{el} to get

$$\varepsilon_{el}^2 = \varepsilon_{el} + \left[\varepsilon_{el} - 1/2\right]\chi(Q)$$

This is a quadratic in ε_{el}. Solving it and keeping the root which gives the correct long wavelength limit we obtain

$$\varepsilon_{el} = \frac{1}{2}\left\{1 + \chi(Q) + \sqrt{1 + \chi^2(Q)}\right\} \tag{3.20}$$

An alternate solution can be obtained as follows. We rewrite eq.(3.15) as

$$\varepsilon_{el} = 1 + \left[1 - \frac{1}{2}\frac{1}{(\varepsilon_{el})}\right]\chi(Q)$$

We have put a circle around the ε_{el} appearing within the brackets. Substituting the value of the other ε_{el} into the circle we obtain

$$\varepsilon_{el} = 1 + \left[1 - \frac{1}{2}\frac{1}{1 + \left[1 - \frac{1}{2}\frac{1}{(\varepsilon_{el})}\right]\chi(Q)}\right]\chi(Q)$$

Continuing this process we get

$$\varepsilon_{el} = 1 + \chi - \frac{\frac{1}{2}\chi}{1 + \chi} - \frac{\frac{1}{2}\chi}{1 + \chi} - \frac{\frac{1}{2}\chi}{1 + \chi} \cdots \tag{3.21}$$

where we have abbreviated $\chi(Q)$ to χ.

This expression is a continued fraction. In fact it is the expansion of eq.(3.20) and thus the same solution in alternate form. Keeping terms up to the second minus sign we get the expression of eq.(3.17), which is thus shown to be an approximation to the solution of eq.(3.15).

6. Exchange Formulae for a Biquadratic Energy Denominator

We will start by discussing the work of Bailyn (B60) and Hone (H60) when the energy function is changed from the parabolic band approximation to the biquadratic form

$$E_{k'} = \frac{\hbar^2 k_F^2}{2m'} (p'x^2 - p'q'x^4) \tag{3.22}$$

We write p' and q' instead of p and q because we will use the symbol q to represent the phonon wave-vector.

Now before we tackle this problem we must make a digression and explain a point of some importance. We go back to the solution of the integral equation

$$v_{Qk} = v_Q^i - \sum_{k'} A(\vec{k}, \vec{k}') v_{Qk'} \tag{3.23}$$

Bailyn solves this as follows. He assumes $v_{Qk'}$ to be independent of $\vec{k}'$ and eliminates the $\vec{k}$ dependence of $A(\vec{k},\vec{k}')$ by averaging over the volume of the Fermi sphere, thus

$$v_Q = \frac{v_Q^i}{1 + \sum_{k'} \left\langle A(\vec{k},\vec{k}') \right\rangle_{vol}} \tag{3.24}$$

Then he substitutes this back into eq.(3.23) to get a second approximation

$$v_{Qk} = v_Q^i \left[\frac{1 + \sum_{k'} \left\langle A(\vec{k},\vec{k}') \right\rangle_{vol} - \sum_{k'} A(\vec{k},\vec{k}')}{1 + \sum_{k'} \left\langle A(\vec{k},\vec{k}') \right\rangle_{vol}} \right] \tag{3.25}$$

He then claims to improve the first approximation by averaging the second approximation over the Fermi surface. The difference between the two averages in the numerator

$$\sum_{k'} \left\langle A(\vec{k},\vec{k}') \right\rangle_{vol} - \sum_{k'} \left\langle A(\vec{k},\vec{k}') \right\rangle_{surf}$$

is described as a significant term. As Hone pointed out this is unjustified, and if the averages are taken consistently (say both over the Fermi surface), then the difference is zero and this just returns us to the first approximation. So we will describe Bailyn's results when both averages are taken over the volume. This yields a simpler expression for $\varepsilon_{el}(Q)$ than the one given by Bailyn.

$$\varepsilon_{el}(Q) = 1 + \frac{\beta F(u)}{2u^2} - \frac{\beta}{4u} \int_{y_o}^{1+2u} 3h(x)x\left[(1+2q'x^2)Q(x,u) + q'R(x,u)\right]dx \qquad (3.26)$$

where y_o, $h(x)$ and $Q(x,u)$ are defined as before

$$F(u) = \frac{1}{p'} f(u) + \frac{q'}{p'}\left[\frac{1-u^4}{4u} \ell n \left|\frac{1+u}{1-u}\right| + \frac{1}{2}u^2 + \frac{3}{2}\right]$$

$$\text{and } R(x,u) = \begin{cases} 8ux & \text{for } x < |2u-1| \\ -1+4u^2 \pm 4ux + x^2 \text{ where } \begin{cases} + \text{ for } x < 1 \\ - \text{ for } x > 1 \end{cases} & \text{for } x > |2u-1| \end{cases}$$

Hone takes surface averages and the corresponding $\varepsilon_{el}(Q)$ can be obtained by replacing $3h(x)$ by $T(x)$ in eq.(3.26)

We now show how some other formulae should be changed when extended to the p'q' energy approximation. The first point to notice is that wherever the function f(u) appears, we should change it to F(u). For example the formula $E' = -\beta T(1) f(u)$ for the exchange and correlation term becomes $E' = -\beta T(1) F(u)$. Now consider the expressions for $\varepsilon_{el}(Q)$ derived in this chapter. The function $X(Q) = \beta f(u)/2u^2$ would become $X(Q) = \beta F(u)/2u^2$. Thus the transition to the p'q' energy approximation can be made quite easily in most cases.

7. Derivation of Takahashi's (T68) Expression

Our starting point is the equation

$$\varepsilon_{el}(Q) = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{\varepsilon_{el} |\vec{k} - \vec{k}'|^2} \right) \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{3.27}$$

For the ε_{el} appearing within the brackets of the right hand side of eq. (3.27) we substitute the first approximation i.e. the Hartree result

$$\varepsilon_{el} = 1 + \frac{\beta f(u')}{2u'^2}$$

where $u' = |\vec{k} - \vec{k}'|/2k_F$

We obtain

$$\varepsilon_{el} = 1 - 4\pi e^2 \sum_{k'} \left(\frac{2}{Q^2} - \frac{1}{u'^2} \left[1 + \frac{\beta f(u')}{2u'^2} \right]^{-1} \right) \frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \tag{3.28}$$

This is essentially Takahashi's result. To obtain the final expression he writes

$$\frac{1}{u'^2}\left[1 + \frac{\beta f(u')}{2u'^2}\right]^{-1} = \sum_{i=1}^{g} \frac{A_i}{B_i + u'^2}$$

where the A_i's and the B_i's are defined by this equation. This permits him to take the average over $\vec{k}$ and then perform the integration over $\vec{k}'$ to obtain

$$\varepsilon_{el} = 1 + \frac{\beta F(u)}{2u^2} - \frac{\beta G(u,h)}{2u^2} \qquad (3.29)$$

The p'q' approximation was used for the energy. $F(u)$ is defined as before and $G(u,h)$ is defined in Takahashi's paper (T68).

8. Summary for Chapter II and III

In chapters II and III various formulae have been derived for $\varepsilon_{el}(Q)$. We have shown that they stem from the same basic equation and are of the type

$$\varepsilon_{el} = 1 + X + E$$

The choice of ε' (to describe electron-electron correlation) was made to various degrees of approximation by different authors. For example the values

$$\begin{cases} \varepsilon' = 1 + k_s^2/|\vec{k}-\vec{k}'|^2 \\ \varepsilon' = 1 + \beta f(u')/2u'^2 \ , \quad u' = |\vec{k}-\vec{k}'|/2k_F \\ \varepsilon' = \varepsilon_{el} \end{cases}$$

were used. Also, in each case, other types of approximations have been made, for example

$$\begin{cases} \text{Averaging over } \vec{k} : \langle \quad \rangle_{avk} = \frac{1}{4\pi}\int d\Omega \\ \text{Hubbard type approx} : |\vec{k}-\vec{k}'|^2_{av} \approx k_F^2 \\ \text{Factorization} : \int \text{SLOW x SINGULAR} = \text{SLOW} \int \text{SINGULAR} \end{cases}$$

In table (3.1) we show which choice of ε' and which approximations were made in the derivation of various authors' ε_{el}.

Author	Choice of ε'	Approximation
Bailyn	$\begin{cases} \infty & \text{for } \lvert\vec{k} - \vec{k}'\rvert < k_c \\ 1 & \text{for } \lvert\vec{k} - \vec{k}'\rvert > k_c \end{cases}$	Volume average over $\vec{k}$
Hone	$1 + k_s^2/\lvert\vec{k} - \vec{k}'\rvert^2$	Surface average over $\vec{k}$
Takahashi	$1 + \beta f(u')/2u'^2$	Average over $\vec{k}$
Hubbard	$1 + k_s^2/\lvert\vec{k} - \vec{k}'\rvert^2$	$\lvert\vec{k} + \vec{k}' - \vec{Q}\rvert^2_{av} \approx k_F^2 + Q^2$
Kleinman	$1 + k_s^2/\lvert\vec{k} - \vec{k}'\rvert^2$	$\lvert\vec{k} + \vec{k}' - \vec{Q}\rvert^2_{av} \approx k_F^2 \div Q^2$ $\lvert\vec{k} - \vec{k}'\rvert^2_{av} \approx k_F^2$
Toya	1 (no screening)	$\lvert\vec{k} - \vec{k}'\rvert^2_{av} \approx k_F^2$
Geldart-Vosko	$1 + k_s^2/\lvert\vec{k} - \vec{k}'\rvert^2$	Factorizing
Ours	$1 + \beta f(u')/2u'^2$ ε_{el}	Factorizing

Table (3.1)

CHAPTER IV

We now turn to the lattice dynamics of sodium, potassium and rubidium. We start by discussing Cochran's method of obtaining empirical effective potentials from the dispersion curves. We work this out to obtain some insight into the problem. Then the method of Cowley et al is applied; a choice of $\epsilon_{el}(Q)$ is made, the pseudopotentials are determined and compared to those obtained by least squares fitting of different models. The dispersion curves are calculated and the interatomic potentials are also obtained.

1. Cochran's (C63) Method of Obtaining Effective Potentials

In the lattice of a metal such as sodium the interactions between ions can be taken to involve (T58, C63)

i) the exchange (overlap) potential V_R (shown by Vosko (V64) to be negligible)

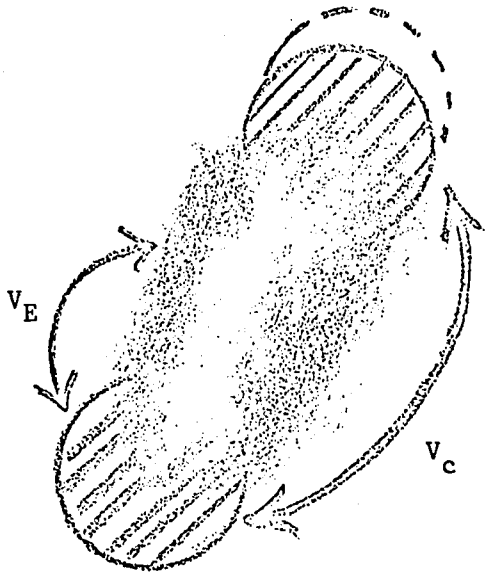
ii) the Coulomb potential V_c

iii) the conduction electron contribution V_E

So, neglecting the overlap, the force acting on any given ion falls into two parts: the force due to the distorted lattice of bare ions (Coulomb) and the electrostatic force due to the electronic charge distribution (The Hellmann-Feynman theorem could be used to calculate this contribution). The Coulomb potential V_c and the electronic contribution V_E must be subtracted to leave a small interatomic potential

$$V = V_c - V_E$$

(V_E is chosen positive by definition)



ion under consideration

The equation for the lattice dynamics of the crystal can be written

$$m\,\omega^2\,U_x(\vec{q}) = \sum_y D_{xy}(\vec{q})\,U_y(\vec{q}) \qquad (4.1)$$

where $D_{xy} = R_{xy} + C_{xy} + E_{xy}$ (4.2)

and
- m the ionic mass
- $\vec{q}$ the phonon wave-vector
- $\vec{U}(\vec{q})$ the polarization vector
- ω the (circular) frequencies

As mentioned earlier, Vosko (V64) shows that the term R_{xy} (due to the overlap forces) is negligible in alkalis. The Coulomb term C_{xy} is

calculated using the Ewald Θ-transformation and the usual formulae for a b.c.c. lattice are given in Appendix E. The conduction-electron term E_{xy} can be written

$$E_{xy}(\vec{q}) = -\sum_{\tau}[(q_x + \tau_x)(q_y + \tau_y)V_E(\vec{q} + \vec{\tau}) - \tau_x\tau_y V_E(\vec{\tau})] \qquad (4.3)$$

where $\vec{\tau}$ is a reciprocal lattice vector and $V_E(Q)$ is the electronic contribution to the interatomic potential. $V_E(Q)$ can be conveniently written as

$$V_E(Q) = \frac{4\pi e^2}{Q^2 v} G_E(Q) \qquad (4.4)$$

where v is the volume of the unit cell and $G_E(0) = 1$. Cochran describes a method to find $G_E(Q)$. The method can be divided into two parts:

First Part: Analyzing the transverse branches which gives us the section of G_E within the range $.866 < \bar{Q} < 1.35$ ($\bar{Q} = Qa/2\pi$).

Second Part: Using these results to analyze the longitudinal branches. That gives us G_E within the range $0 < \bar{Q} < 1$.

As an example of the treatment given to the transverse branches we shall discuss the case when $\vec{q}$ is parallel to $[1,0,0]$. We have

$$m\omega^2 = D_{yy}(\vec{q}) \qquad (4.5)$$

$$= C_{yy}(\vec{q}) + E_{yy}(\vec{q})$$

Cochran uses the units e^2/v and writes eq.(4.5) as

$$m\omega^2 = (e^2/v)N \qquad (4.6)$$

where the dimensionless number N can be divided into two contributions N_c and N_E , so eq.(4.6) becomes

$$m\,\omega^2 v/e^2 = N_c + N_E$$

Subtracting the known contribution N_c from $m\,\omega^2 v/e^2$ we obtain what may be regarded as empirical values of N_E. Using the expression for E_{xy} as given by eqs.(4.3) and (4.4) we obtain

$$N_E(\vec{q}) = N_E(-\vec{q}) = -4\pi \sum_{\tau} \frac{(\tau_y - q_y)^2}{(\vec{\tau} - \vec{q})^2} G_E(\vec{\tau} - \vec{q}) \qquad (4.7)$$

Cochran assumes that $G_E(Q)$ falls to a very small value for $\bar{Q} = Qa/2\pi > \sqrt{2}$ (thus the term $G_E(\vec{\tau})$ is missing in eq.(4.7)). With this assumption the only lattice points to be considered in the sum of eq.(4.7) are those shown in fig.(4.1). Table (4.1) shows how they add up.

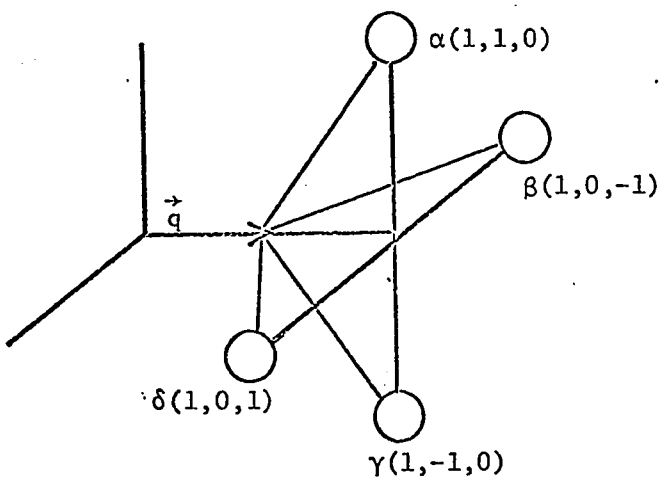


fig.(4.1)

	$\bar{\tau}_y$	$\bar{\tau}_y - \bar{q}_y$	$(\bar{\tau}_y - \bar{q}_y)^2$
α	1	1	1
β	0	0	0
γ	-1	-1	1
δ	0	0	0
TOTAL			2

Table (4.1)

where $\vec{\tau} = \frac{2\pi}{a} (\bar{\tau}_x, \bar{\tau}_y, \bar{\tau}_z)$

and $\vec{q} = \frac{2\pi}{a} (\bar{q}_x, \bar{q}_y, \bar{q}_z)$

So eq.(4.7) becomes

$$N_E(\vec{q}) = - \frac{8\pi}{(\vec{\tau} - \vec{q})^2} G_E(\vec{\tau} - \vec{q}) \qquad (4.8)$$

Now for the case under consideration $(\vec{\tau} - \vec{q})^2 = (1 - \zeta)^2 + 1$

where $\zeta = \bar{q}_x$, so that eq.(4.8) yields

$$G_E(\vec{\tau} - \vec{q}) = - \frac{(1 - \zeta)^2 + 1}{8\pi} N_E(\vec{q}) \qquad (4.9)$$

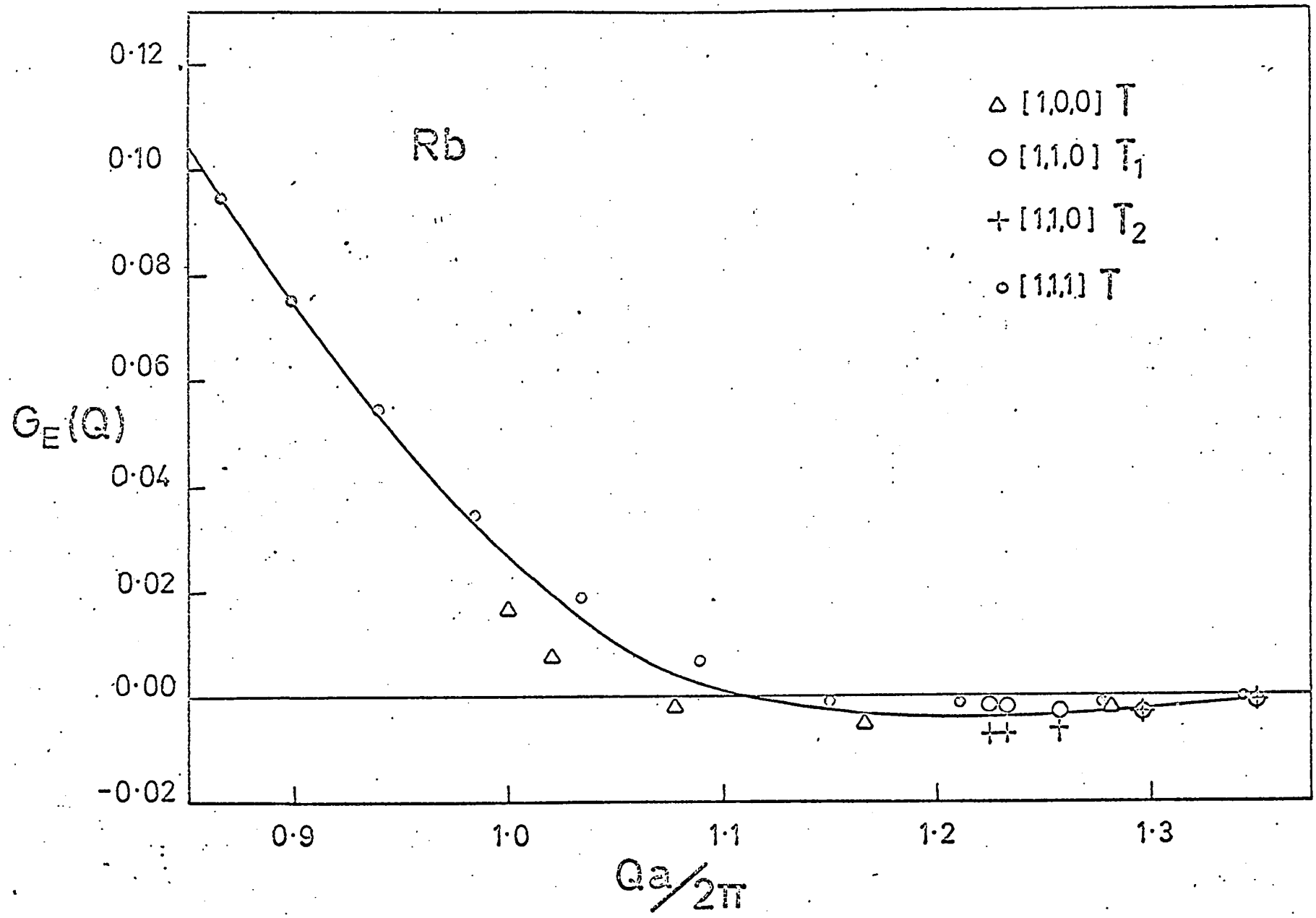


Fig.(4.2) The tail portion of G_E for rubidium.

Each transverse branch yields an equation such as this. The set of equations yields values of G_E for the range $.86 < \bar{Q} < 1.35$. The results are unique for sodium but for potassium and rubidium different branches give different curve segments. Fig.(4.2) shows the tail portion of G_E obtained for rubidium (the scale is much enlarged). Also G_E should be non-negative for all values of Q but we see that this is not the case for rubidium. These facts show that a larger number of reciprocal lattice points should be used. But before we describe the other method, we will show how the remaining portion of G_E is determined. As mentioned the longitudinal branches are used and we will consider the case with $\vec{q}$ parallel to $[1,1,1]$. We have

$$m\omega^2 = D_{xx}(\vec{q}) + 2\, D_{xy}(\vec{q}) \tag{4.10}$$

The corresponding equation for N_E can be written as

$$N_E(\vec{q}) = -\, 4\pi \sum_{\tau} \frac{(\tau_x - q_x)^2 + 2(\tau_x - q_x)(\tau_y - q_y)}{(\vec{\tau}-\vec{q})^2}\, G_E(\vec{\tau}-\vec{q}) \tag{4.11}$$

Apart from the point $\vec{\tau} = 0$, only three other points contribute to the sum. They are shown in fig.(4.3) and table (4.2) shows how they add up.

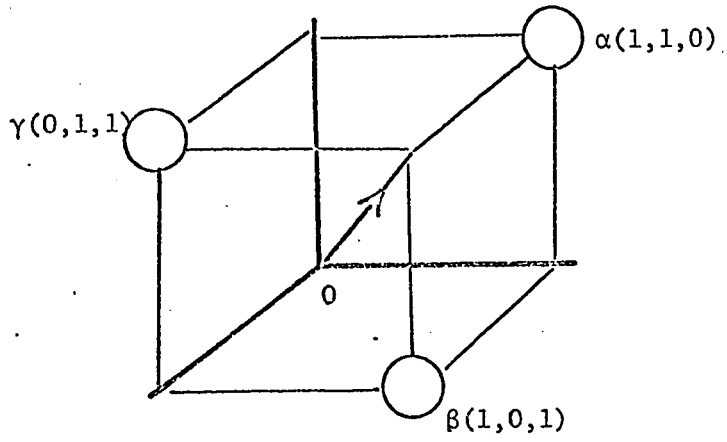


fig.(4.3)

	point	$\bar{\tau}_x$	$\bar{\tau}_y$	$\bar{\tau}_x - \bar{q}_x$	$(\bar{\tau}_x - \bar{q}_x)^2 + 2(\bar{\tau}_x - \bar{q}_x)(\bar{\tau}_y - \bar{q}_y)$
$\vec{\tau} = 0$	0	0	0	$-\zeta$	$3\zeta^2$
	α	1	1	$1-\zeta$	$3 - 6\zeta + 3\zeta^2$
$\vec{\tau} \neq 0$	β	1	0	$1-\zeta$	$1 - 4\zeta + 3\zeta^2$
	γ	0	1	$-\zeta$	$-2\zeta + 3\zeta^2$
Total for $\vec{\tau} \neq 0$					$4 - 12\zeta + 9\zeta^2$

Table (4.2)

where $\zeta = \bar{q}_x = \bar{q}_y$, and we also have

for $\vec{\tau} = 0$ $\quad (\vec{\bar{\tau}} - \vec{\bar{q}})^2 = 3\zeta^2$

for $\vec{\tau} \neq 0$ $\quad (\vec{\bar{\tau}} - \vec{\bar{q}})^2 = 2(1 - \zeta)^2 + \zeta^2$

so that eq. (4.11) becomes

$$N_E(\vec{q}) = -4\pi \left[G_E(\vec{q}) + \frac{(2 - 3\zeta)^2}{2(1 - \zeta)^2 + \zeta^2} G_E(\vec{\tau} - \vec{q}) \right] \qquad (4.12)$$

So knowing $G_E(\vec{\tau} - \vec{q})$ from the analysis of the transverse branches $G_E(\vec{q})$ can be determined. The procedure is as follows: eq.(4.12) can be written

$$G_E(\vec{q}) = -\frac{N_E(\vec{q})}{4\pi} - (2 - 3\zeta)^2 \frac{G(\xi)}{\xi^2} \qquad (4.13)$$

where $\xi^2 = 2(1 - \zeta)^2 + \zeta^2$

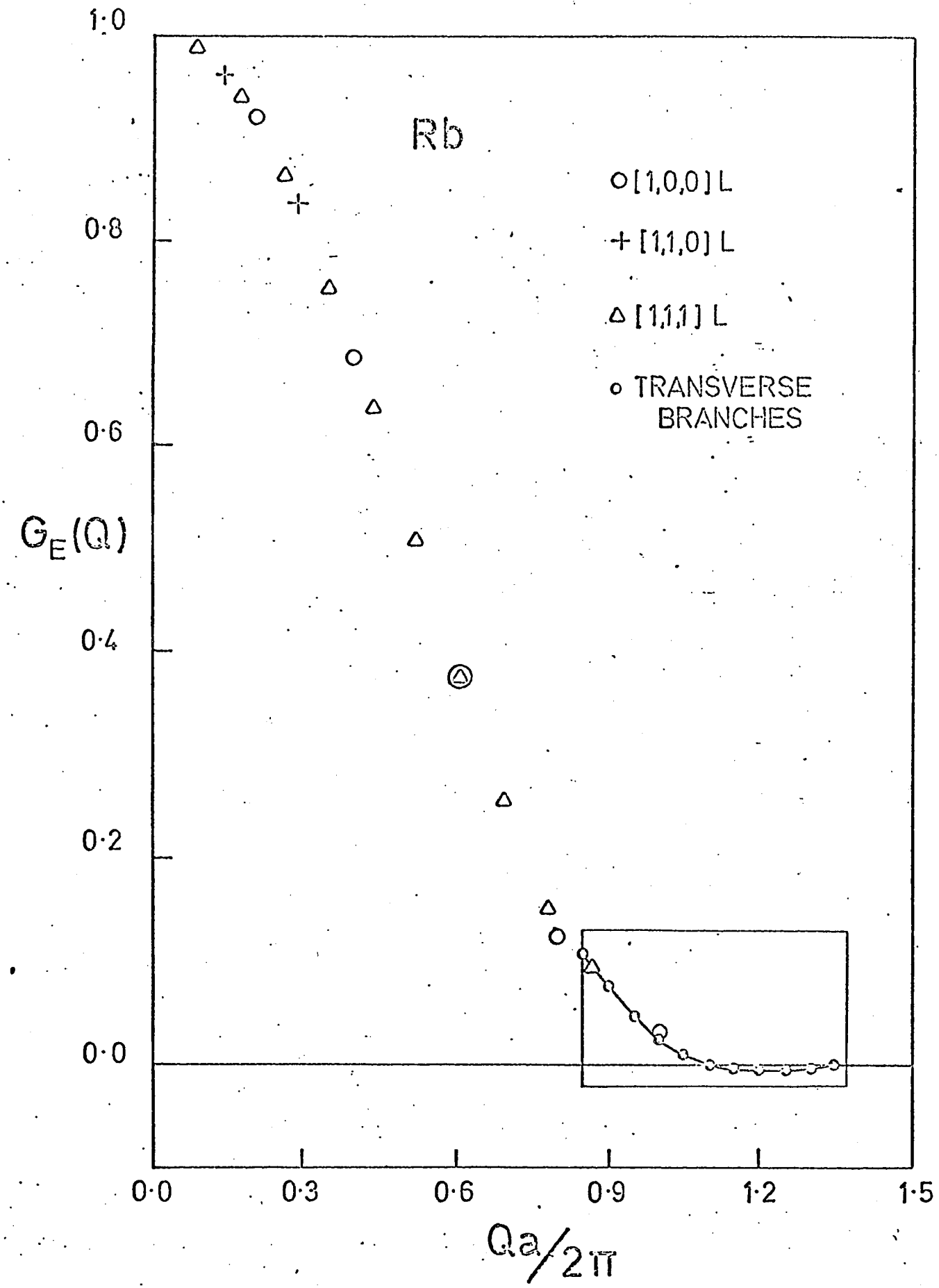


Fig.(4.4) G_E over the range considered by Cochran.

$G(\xi)$ is obtained from a smooth curve drawn through the points obtained from the transverse branches. (Lagrange interpolation is used with a table of values.) The longitudinal branches yield a set of equations such as (4.13). From these G_E is obtained for the range $0 < \bar{Q} < 1$. Combining these results with those of the transverse branches G_E is specified over the range considered by Cochran. Fig.(4.4) shows G_E for rubidium. The area enclosed by a rectangle shows the region determined by the transverse branches. It overlaps with the one of the longitudinal branches.

2. The Method of Cowley et al (C66) for Obtaining the Local Pseudopotential

Cowley, Woods and Dolling (C66) assume a local pseudopotential for the conduction electron-ion interaction. Let $V_p(Q)$ be the Fourier transform of the local pseudopotential and $\varepsilon_{pr}(Q)$ the "proton-proton" dielectric function (see Appendix F), we have

$$V_E(Q) = \left(\frac{vQ^2}{4\pi e^2}\right)\left(1 - \frac{1}{\varepsilon_{pr}(Q)}\right)|V_p(Q)|^2 \qquad (4.13)$$

$V_p(Q)$ can be written as

$$V_p(Q) = -\frac{4\pi e^2}{vQ^2} f(Q)$$

where $f(Q)$ is the form factor, one convenient property of the form factor is that $f(0) = 1$. The relationship between the previously defined $G_E(Q)$ and $f(Q)$ is

$$G_E(Q) = f^2(Q)\left(1 - \frac{1}{\varepsilon_{pr}(Q)}\right) \qquad (4.15)$$

or, alternatively

$$G_E(Q) = \mathcal{f}^2(Q) \frac{\chi(Q)}{\varepsilon_{el}(Q)} \qquad (4.16)$$

where $\varepsilon_{pr}(Q)$ and $\varepsilon_{el}(Q)$ are the "proton-proton" and the "proton-electron" dielectric constants respectively (see Appendix F for the relationship between them). For the choice of the dielectric constants we take our formulae

$$\varepsilon_{el}(Q) = 1 + \left[1 - \frac{1}{2} \frac{1}{1 + \chi(Q)} \right] \chi(Q)$$

and

$$\varepsilon_{el}(Q) = \frac{1}{2} \left\{ 1 + \chi(Q) + \sqrt{1 + \chi^2(Q)} \right\}$$

We feel that these formulae are better than the others because of

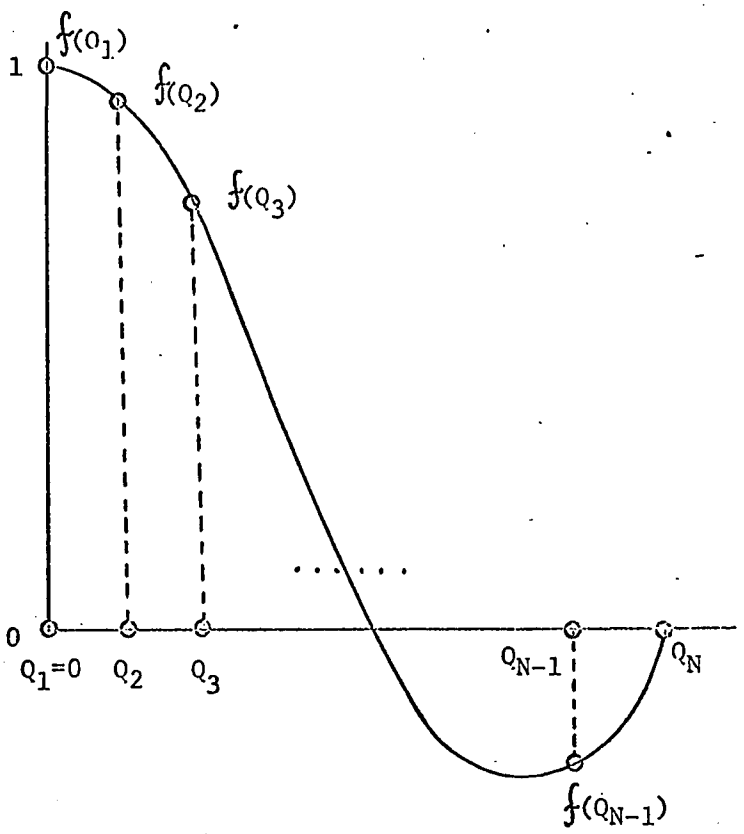
1) a better description of electron-electron correlation (choice $\varepsilon' = \varepsilon_{el}$).

2) the justification given to the factorization procedure used in their derivation.

3) they involve no free parameter (no parameter k_s which can change the magnitude of the exchange and correlation term by a factor as large as three, depending on the choice made (fig.(3.10))).

We now describe how $\mathcal{f}(Q)$ is obtained. The general shape is known from previous work such as Cochran's or Cowley et al's. We know that $\mathcal{f}(Q_1) = 1$ for $Q_1 = 0$. We chose a Q_N such that $G_E(Q)$ is negligible beyond this limit and set $\mathcal{f}(Q_N) = 0$. We then specify $\mathcal{f}$ at the points

Q_2, Q_3, ..., Q_{N-1}. Values at intermediate points are found by Lagrange (cubic) interpolation.



This is used as the first stage of a non linear least squares procedure where $f(Q_2)$, $f(Q_3)$, ..., $f(Q_{N-1})$ are used as the variable parameters C_1, C_2, ..., C_M of the least squares fit. The problem then reduces to determining the set of parameter values which minimizes the quantity

$$\Delta = \sum_i \left[\omega_{exp,i} - \omega(\vec{q}_i, C_1, C_2, \ldots, C_M)\right]^2 \qquad (4.17)$$

	Na		K		Rb	
$\bar{Q} = \frac{Qa}{2\pi}$	$\mathcal{J}(\bar{Q})$	$G_E(\bar{Q})$	$\mathcal{J}(\bar{Q})$	$G_E(\bar{Q})$	$\mathcal{J}(\bar{Q})$	$G_E(\bar{Q})$
.2	.968	.918	.962	.911	.967	.921
.4	.878	.703	.854	.678	.857	.687
.6	.735	.430	.689	.395	.673	.382
.8	.539	.187	.465	.151	.465	.155
1.0	.301	.043	.211	.024	.213	.025
1.2	.056	.001	-.057	.001	-.001	.000
1.4	-.130	.002	-.281	.014	-.183	.006
1.6	-.195	.003	-.402	.016	-.267	.008
1.8	-.091	.000	-.462	.013	-.227	.003
2.0	0	0	-.435	.008	-.196	.002
2.2			-.399	.004	0	0
2.4			-.250	.001		
2.6			0	0		

table (4.3)

this table comes from the calculations with the EC term $E_3 = -\frac{1}{2}\frac{\chi}{1+\chi}$

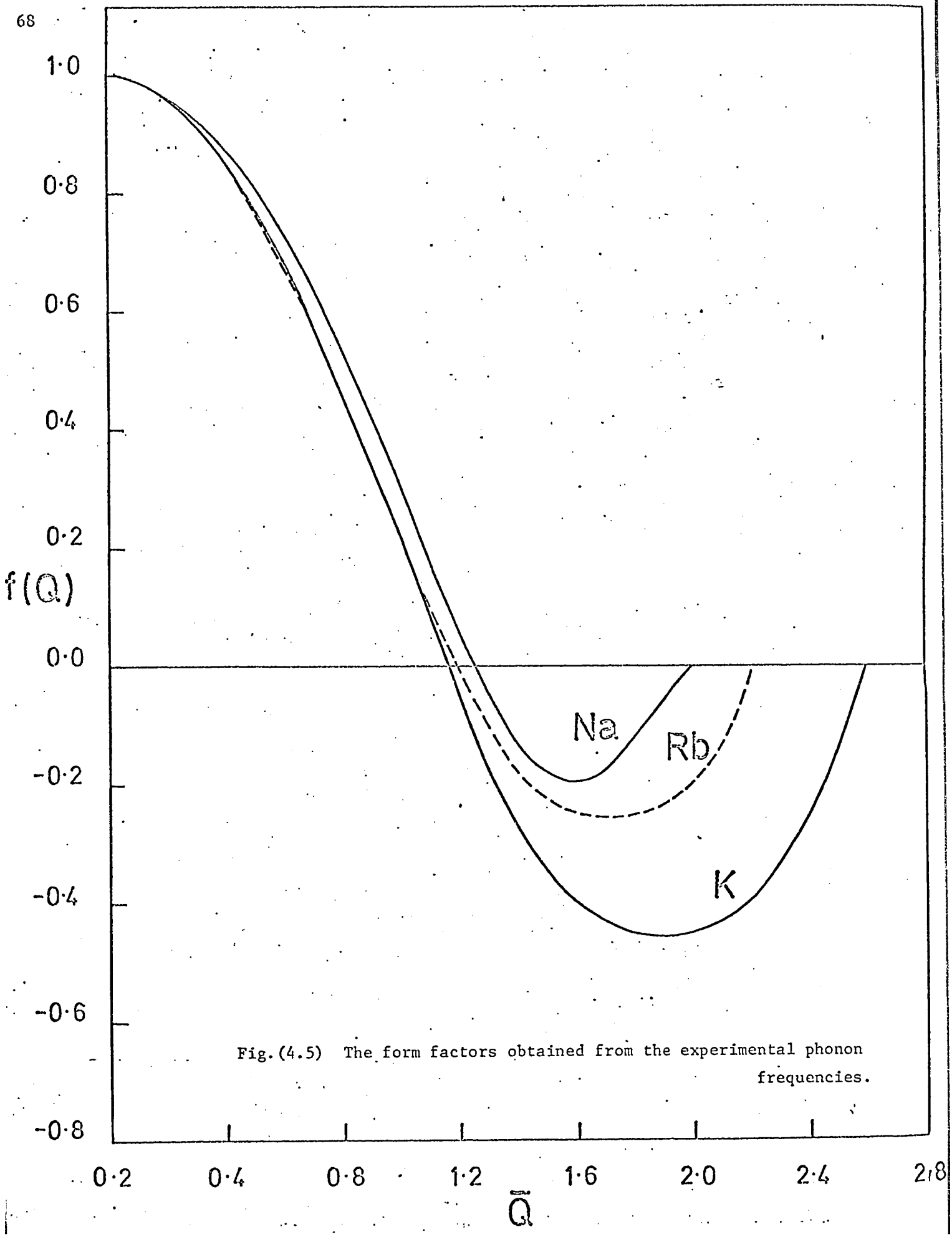


Fig.(4.5) The form factors obtained from the experimental phonon frequencies.

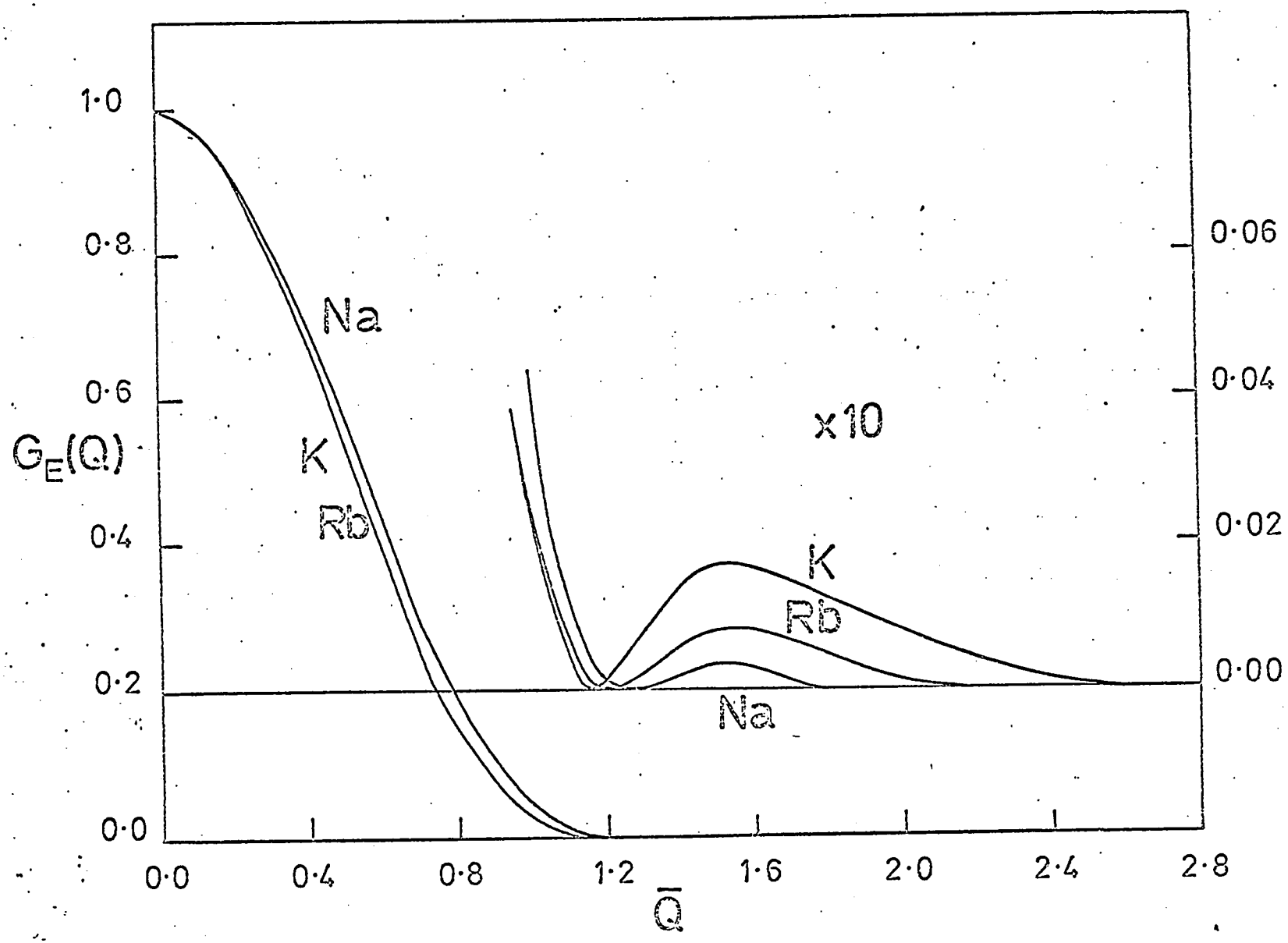


Fig.(4.6) The $G_E(Q)$'s obtained from the experimental phonon frequencies.

where $\omega_{exp,i}$ is an experimental value and $\omega(\vec{q}_i, C_1, C_2, \ldots, C_M)$ a computed one. The details of the method are given in Appendix G.

The form factors $f(Q)$ thus obtained are plotted in fig.(4.5). Smooth curves were drawn through the points obtained from the least squares fit, they are tabulated in table (4.3). Eleven points were used to fit sodium, fourteen points for potassium and twelve points for rubidium. The number of points used depended on the size of the tail obtained. We see that Na has a small tail in comparison to K and Rb. This difference is reflected in the $G_E(Q)$ curves which are plotted in fig.(4.6). An enlarged scale is used for the range $\bar{Q} \geq 1$. The difference between the G_E curve for K and Rb cannot be seen on the scale used for the range $0 \leq \bar{Q} \leq 1$.

Homology

It is interesting to compare the experimental dispersion curves of Na, K and Rb by computing the reduced frequencies

$$\omega_r = \omega/\omega_p$$

where $\omega_p = \sqrt{\frac{4\pi e^2}{vm}}$ is the plasma frequency of the ions. For example choosing the point $q = q_{max}$ in the $[1,0,0]$ direction we get

$$\text{for Na} \quad \omega_r = .503$$

$$\text{for K} \quad \omega_r = .554$$

$$\text{for Rb} \quad \omega_r = .544$$

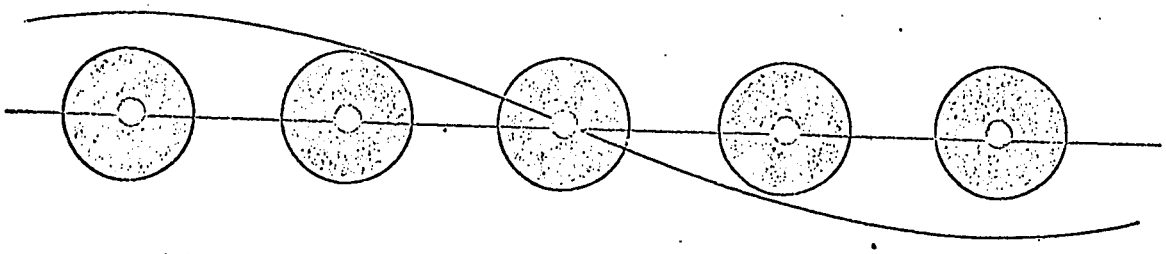
There is roughly 9% difference between Na and K, 2% between K and Rb and 7% between Na and Rb.

In these natural units the Coulomb contribution is the same for Na, K and Rb and the conduction electron term $\bar{E}_{xy}$ is given (also in reduced units) by

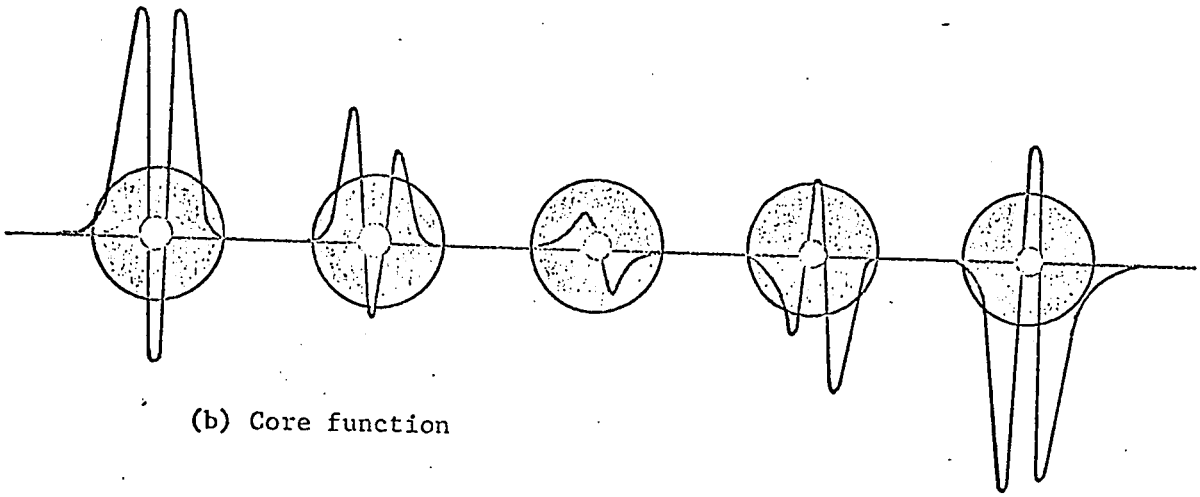
$$\bar{E}_{xy}(\vec{q}) = -\sum_{\tau}\left[\frac{(\tau_x+q_x)(q_y+\tau_y)}{(\vec{\tau}+\vec{q})^2}G_E(\vec{q}+\vec{\tau}) - \frac{\tau_x\tau_y}{\tau^2}G_E(\vec{\tau})\right]$$

So in these natural units, two sets of dispersion curves coincide when the corresponding G_E curves coincide. Therefore the dispersion curves of Na, K and Rb are not homologous in the above sense, since their G_E curves show different characteristics. The differences will be further brought out when the interatomic potentials are calculated.

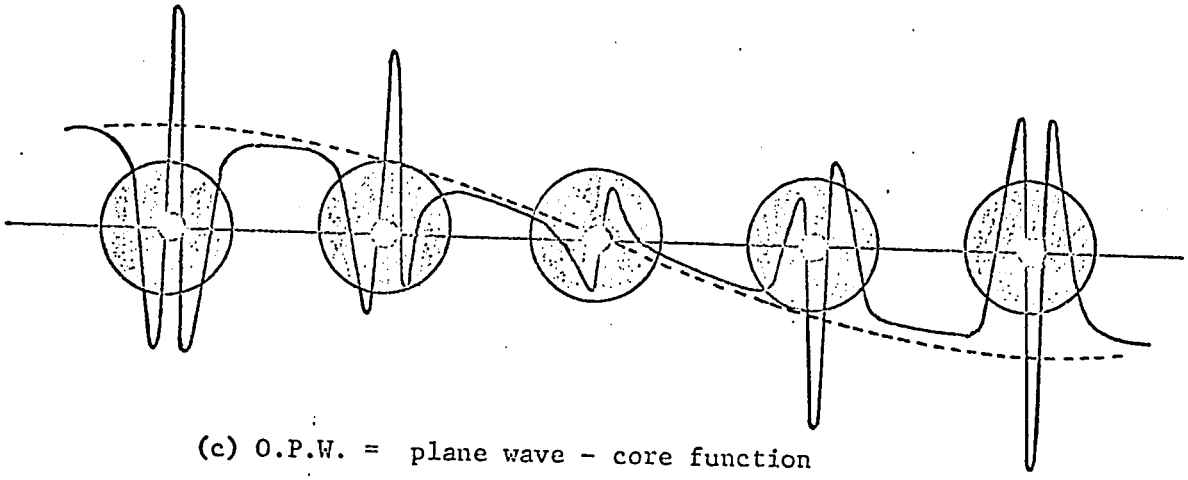
One can also define homology in the following more general sense. The ratio $\omega_A(\vec{q}_i)/\omega_B(\vec{q}_i)$ for pairs (A,B) of elements should be constant (within the limits of experimental errors) for the values $\vec{q}_i$ common to both sets of data. Copley, Brockhouse and Chen (C68) have found that there seems to be a definite departure from homology (in the above sense) especially for Na and Rb.



(a) Plane wave



(b) Core function



(c) O.P.W. = plane wave - core function

Fig.(4.7) Synthesis of an orthogonalized plane wave.

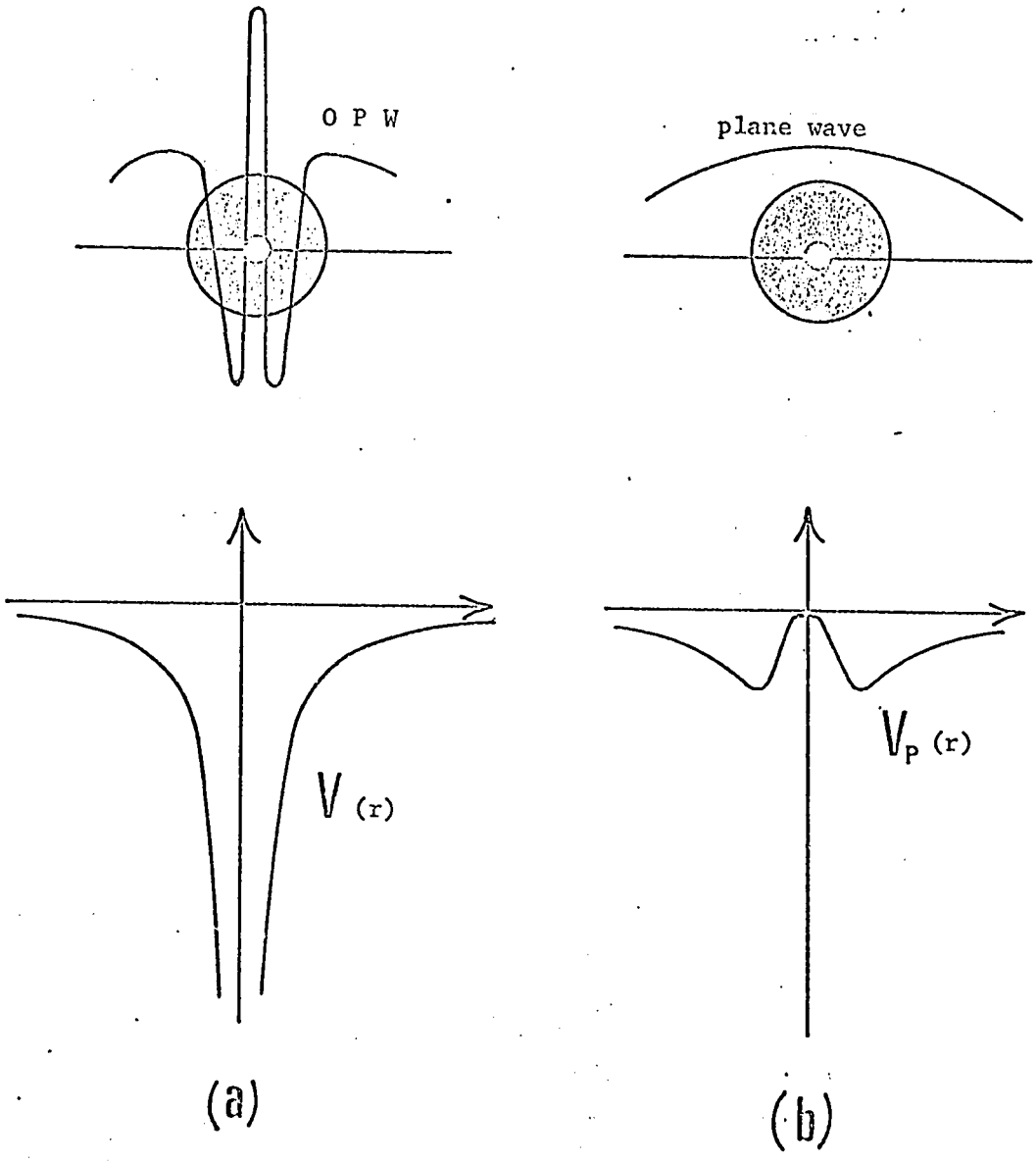


Fig.(4.8) An O.P.W. in the true potential (a) can be replaced by a simple plané wave in the effective potential (b).

3. Some Model Pseudopotentials

The concept of the pseudopotential in a metal comes from the following argument (Z62). The wave-function of a conduction electron in a metal can be represented by orthogonalized plane waves (OPW's). An OPW is the combination of a plane wave $\exp(i\vec{k}\cdot\vec{r})$ with an appropriate mixture of states constructed out of the ion core wave-functions, the mixture being chosen to be exactly orthogonal to these core states. Each OPW is a very good representation of the sort of wave-function that an electron must have in a metal. The core wave-functions are compact and vanish outside the closed shells of the ions. Thus in the interstitial region an OPW looks very much like a plane wave, but in the core it can have plenty of oscillations and looks very much like the wave-function for the next atomic state above the closed shell (see fig.(4.7) which is taken from Z62).

The main point is that an OPW in the ionic potential (which is very strong with a singularity like $-ze^2/r$ near the nucleus) is equivalent to a simple plane wave in a rather weak effective potential (fig.(4.8) taken from Z62), because the orthogonality condition can be made to look like a strong repulsive potential which cancels the singularity in the ionic potential. The net effective potential is thus quite small, this is what we call the pseudopotential V_p. We will now describe some models for the pseudopotential.

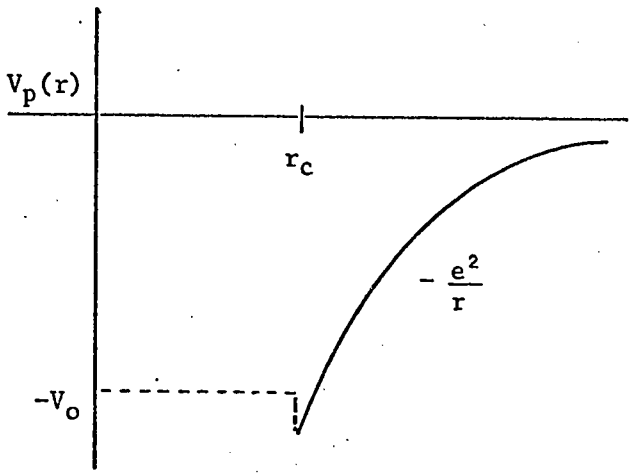
The Heine-Abarenkov (H64) Model

Following Ho (H68) we adopt a simplified version of the Heine-

Abarenkov model. It is given by

$$V_p(r) = \begin{cases} -V_o & \text{for } r < r_c \\ -\frac{e^2}{r} & \text{for } r > r_c \end{cases} \qquad (4.18)$$

where r_c is a measure of the effective core radius and V_o is the core potential. The assumption that V_o is constant implies that the potential is a local pseudopotential.



The form of this pseudopotential is plausible since we know that the singularity of the Coulomb potential should be cancelled, leaving a small effective potential inside the core while the potential outside the core is essentially unaltered.

Let us first consider the special case $V_o = 0$. The Fourier transform of V_p is given by

$$V_p(Q) = -\frac{4\pi e^2}{v\,Q^2}\cos(Qr_c) \qquad (4.19)$$

$$= -\frac{4\pi e^2}{v\,Q^2}\,f(Q)$$

We see that the Fourier transform of V_p is equal to the Fourier transform $-\frac{4\pi e^2}{v\,Q^2}$ of the Coulomb potential times the form factor $f(Q) = \cos(Qr_c)$. Ashcroft (A68) used this potential to calculate the phonon spectra of Na and K.

Now the case $V_o \neq 0$ yields

$$V_p(Q) = -\frac{4\pi}{vQ^2}\left[\frac{V_o \sin(Qr_c)}{Q} + (e^2 - V_o r_c)\cos(Qr_c)\right] \qquad (4.20)$$

$$= -\frac{4\pi e^2}{vQ^2}\,f_{Ho}(Q)$$

where $f_{Ho}(Q) = \cos(Qr_c) + A\,Q^2 g(Qr_c)$ (4.21)

with $A = \frac{r_c^3 V_o}{3e^2}$ and $g(x) = 3(\sin x - x\cos x)/x^3$

(since this pseudopotential was used by Ho (H68) we shall refer to the corresponding form factor as $f_{Ho}(Q)$). A and r_c will be treated as adjustable parameters.

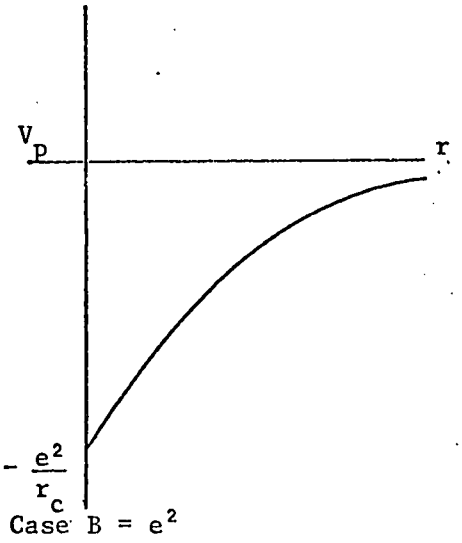
The Hellmann (H35, H36) Pseudopotential

The Hellmann pseudopotential can be written

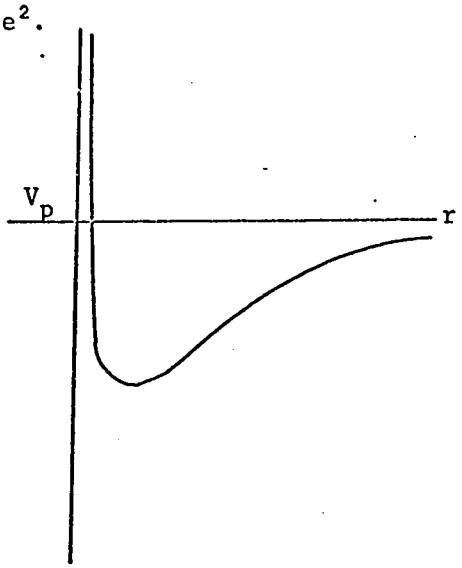
$$V_p(r) = -\frac{e^2}{r} + \frac{B}{r}\exp(-r/r_c) \qquad (4.22)$$

where r_c is a parameter analogous to the effective core radius, the term $\frac{B}{r}\exp(-r/r_c)$ is the repulsive part of the pseudopotential and the parameter B controls the degree of cancellation of the Coulomb singularity. We see that the exponential factor $\exp(-r/r_c)$ makes V_p essentially a Coulomb potential outside the range of the effective "radius" r_c.

The best cancellation of the Coulomb singularity occurs for $B = e^2$. This is plotted below, alongside the case $B > e^2$.



Case $B = e^2$



Case $B > e^2$

The Fourier transform of V_p is given by

$$V_p(Q) = -\frac{4\pi e^2}{vQ^2} + \frac{4\pi B}{v}\frac{r_c^2}{1 + (Qr_c)^2} \qquad (4.23)$$

$$= - \frac{4\pi e^2}{vQ^2} \mathcal{f}_{Hel}(Q)$$

where $\mathcal{f}_{Hel}(Q) = 1 - \frac{AQ^2}{1 + (Qr_c)^2}$ (4.24)

with $A = \frac{Br_c^2}{e^2}$, A and r_c will be treated as adjustable parameters.

Harrison's (H66) Pseudopotential

Harrison suggested a simple form for V_p

$$V_p(r) = - \frac{e^2}{r} + B\delta(r) \qquad (4.25)$$

The repulsive part is represented by a δ function at the nucleus, B is the strength of the repulsion and is left as an adjustable parameter. The Fourier transform of V_p is given by

$$V_p(Q) = - \frac{4\pi e^2}{vQ^2} + \frac{B}{v} \qquad (4.26)$$

We see that for large Q, $V_p(Q)$ approaches a constant, whereas it should drop to zero. Harrison overcomes the shortcoming of this point ion model by examining the Austin-Heine-Sham form of the pseudopotential where the repulsive part is found to decay as $\frac{1}{\left[1 + (Qr_c)^2\right]^2}$ where r_c is of the order of the Bohr radius.

Thus $V_p(Q)$ becomes

$$V_p(Q) = -\frac{4\pi e^2}{vQ^2} + \frac{B/v}{\left[1 + (Qr_c)^2\right]^2} \qquad (4.27)$$

$$= -\frac{4\pi e^2}{vQ^2} \mathcal{F}_{Har}(Q)$$

where $\mathcal{F}_{Har}(Q) = 1 - \frac{AQ^2}{\left[1 + (Qr_c)^2\right]^2}$ (4.28)

with $A = \frac{B}{4\pi e^2 v}$, A and r_c will be treated as adjustable parameters.

The Bardeen (B37) Pseudopotential

The Bardeen pseudopotential is given by

$$V_p(r) = \begin{cases} -\left(\frac{3e^2}{2r_s} - \frac{e^2 r^2}{2r_s^3} + U_o\right) & \text{for } r < r_s \\ -\frac{e^2}{r} & \text{for } r > r_s \end{cases} \qquad (4.29)$$

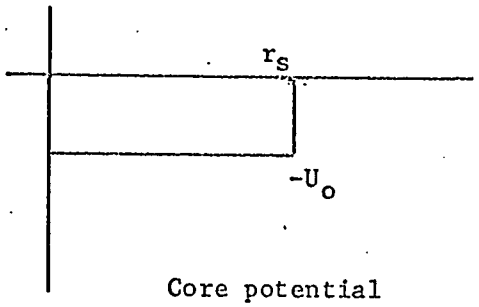
where r_s is the radius of the Wigner-Seitz sphere.

The interpretation of this pseudopotential has been given by Sham and Ziman (S63). It is made up of two contributions.

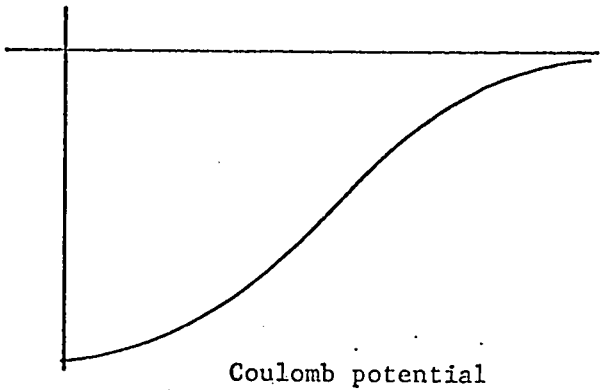
1) An effective potential to represent the core. This is taken to be a square well of radius r_s and strength U_o.

2) The Coulomb potential of the valence electron e removed from the neutral atom to make it an ion. This is taken to be the electrostatic

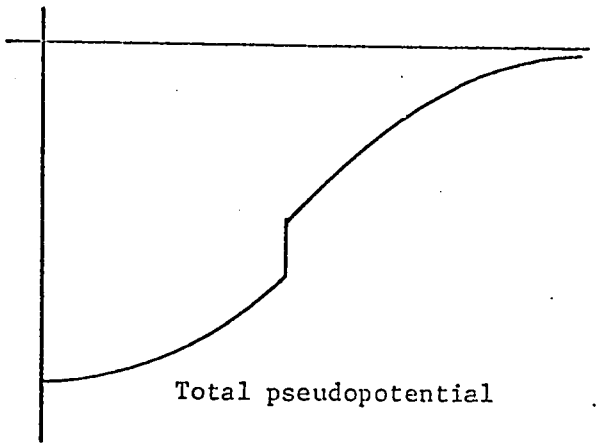
field of the charge $|e|$ spread uniformly over the sphere of radius r_s.



Core potential



Coulomb potential



Total pseudopotential

The Fourier transform of the Bardeen pseudopotential is given by

$$V_p(Q) = -\left\{\frac{4\pi e^2}{vQ^2} + U_o\right\} g(Qr_s) \qquad (4.30)$$

$$= -\frac{4\pi e^2}{vQ^2} f_{Bar}(Q)$$

where $f_{Bar}(Q) = (1 + AQ^2)\ g\ (Qr_s)$ (4.31)

with $A = \frac{vU_o}{4\pi e^2}$, $g(x) = 3(\sin x - x \cos x)/x^3$. A and r_s are treated as adjustable parameters.

4. Calculation of the Phonon Dispersion Curves

We will now use the model pseudopotentials of the last section in conjunction with various exchange and correlation (EC) terms, to calculate the phonon dispersion curves of Na, K and Rb. The form factors will be written in terms of $\bar{Q}$, this will involve a redefinition of the model parameters.

$$f_{Ho}(\bar{Q}) = \cos(\bar{Q}r_c') + A'\bar{Q}^2 g(\bar{Q}r_c')$$

$$f_{Hel}(\bar{Q}) = 1 - \frac{A'\bar{Q}^2}{1 + (\bar{Q}r_c')^2}$$

$$f_{Har}(\bar{Q}) = 1 - \frac{A'\bar{Q}^2}{\left[1 + (\bar{Q}r_c')^2\right]^2}$$

$$f_{Bar}(\bar{Q}) = (1 + A'\bar{Q}^2)g(\bar{Q}r_s')$$

where $\bar{Q} = \frac{Qa}{2\pi}$, $r_c' = \frac{2\pi}{a} r_c$, $r_s' = \frac{2\pi}{a} r_s$, $A' = \left(\frac{2\pi}{a}\right)^2 A$

and a is the lattice constant.

We will also use empirical pseudopotentials, chosen such that their form factors reproduce the shape of the empirically derived form factors of section 2 of this chapter. Some of the form factors tried are listed below.

$$f_1(Q) = (1 + \alpha Q^2 + \beta Q^4) \frac{\sin \gamma Q}{\gamma Q}$$

$$f_2(Q) = \frac{(1 + \alpha Q^2 + \beta Q^4)}{1 + \gamma Q^6}$$

$$f_3(Q) = \frac{(1 + \alpha Q^2 + \beta Q^4 + \gamma Q^6)}{1 + \gamma Q^8}$$

$$f_4(Q) = (1 + \alpha Q^2 + \beta Q^4)g(\gamma Q)$$

To write these form factors in terms of $\bar{Q}$, change α, β and γ to α', β' and γ'.

Four dielectric constants were used in conjunction with the model pseudopotentials, they are given by

$$\varepsilon_{el}(Q) = 1 + \chi + E_i \qquad i = 1,\ldots,4$$

where the EC terms are

$$E_1 = -\beta T(1) f(u) \qquad \text{derived from Hone's formulation}$$

$$E_2 = -\frac{\beta f(u)}{4u^2 + x_o^2} \qquad \text{Geldart-Vosko's}$$

$$\left.\begin{aligned} E_3 &= -\frac{1}{2}\frac{\chi}{1+\chi} \\ E_4 &= -\frac{1}{2}\left\{1 + \chi - \sqrt{1 + \chi^2}\right\} \end{aligned}\right\} \qquad \text{our formulae}$$

The first two EC expressions contain the parameter x_o which is treated as adjustable.

Results

The parameters were determined by fitting the computed frequencies to the experimental frequencies by the method of non-linear least squares. This consists in minimizing expressions such as

$$\Delta = \sum_i \left[\omega_{exp,i} - \omega(\vec{q}_i, A', r_c')\right]^2$$

The results are listed in tables (4.4), (4.5), (4.6) and (4.7). The parameter set for any combination of pseudopotential and EC term is found by looking up the corresponding row and column.

The results for the EC terms containing the parameter $x_o = k_s/k_F$ were considered acceptable when k_s stayed within the range $.5k_F \lesssim k_s \lesssim 2k_F$. Values outside this range were considered too far from the physically possi-

SODIUM

MODEL / EC term		Harrison	Hellmann	Bardeen	Ho
$\frac{-\beta f(u)}{4u^2 + x_o^2}$	A'	$.89_6$	$.87_9$	$.66_6$	$.28_2$
	r_c'	$.36_7$	$.53_8$	3.60_1	1.52_7
	x_o	1.40	1.54	.53	1.41
	d	$.015_6$	$.014_3$	$.015_2$	$.014_1$
$-\frac{1}{2}\frac{X}{1+X}$	A'	$.87_3$	$.87_4$	$.54_2$	$.20_1$
	r_c'	$.35_3$	$.53_1$	3.56_7	1.46_1
	d	$.015_7$	$.014_o$	$.009_7$	$.014_2$
$\frac{1}{2}\left\{-1 - X + \sqrt{1+X^2}\right\}$	A'	$.88_6$	$.88_9$	$.52_4$	$.21_9$
	r_c'	$.35_8$	$.54_2$	3.56_8	1.48_o
	d	$.014_9$	$.013_3$	$.008_8$	$.013_1$

table (4.4)

the symbol r_c' means r_s' in the case of Bardeen's model

POTASSIUM

MODEL / EC term		Harrison	Hellmann	Bardeen	Ho
$\frac{-\beta f(u)}{4u^2 + x_o^2}$	A'	1.07_7	1.10_0	$.75_7$	$.14_5$
	r_c'	$.41_3$	$.65_5$	3.77_9	1.51_4
	x_o	1.40	1.43	.80	1.66
	d	$.014_3$	$.015_6$	$.006_4$	$.009_5$
$-\frac{1}{2}\frac{\chi}{1+\chi}$	A'	1.04_7	1.06_2	$.55_7$	$.14_3$
	r_c'	$.39_9$	$.62_4$	3.77_4	1.51_3
	d	$.014_7$	$.015_6$	$.008_3$	$.008_6$
$\frac{1}{2}\left\{-1-\chi + \sqrt{1+\chi^2}\right\}$	A'	1.03_7	1.05_1	$.56_5$	$.13_5$
	r_c'	$.39_6$	$.61_7$	3.76_7	1.50_4
	d	$.015_3$	$.016_0$	$.008_7$	$.009_2$

table (4.5)

the symbol r_c' means r_s' in the case of Bardeen's model

RUBIDIUM

MODEL / EC term		Harrison	Hellmann	Bardeen	Ho
$\frac{-\beta f(u)}{4u^2 + x_o^2}$	A'	1.14_3	1.20_2	$.52_3$	$.52_8$
	r_c'	$.44_o$	$.72_8$	3.75_3	1.77_3
	x_o	1.21	1.17	1.85	1.41
	d	$.011_6$	$.012_9$	$.007_5$	$.007_4$
$-\frac{1}{2}\frac{X}{1+X}$	A'	1.05_9	1.07_4	$.52_1$	$.40_o$
	r_c'	$.40_6$	$.63_5$	3.75_6	1.68_5
	d	$.015_8$	$.016_o$	$.007_6$	$.010_2$
$\frac{1}{2}\left\{-1 - X + \sqrt{1+X^2}\right\}$	A'	1.06_7	1.08_4	$.51_2$	$.41_5$
	r_c'	$.40_9$	$.64_1$	3.76_2	1.69_7
	d	$.015_6$	$.016_1$	$.007_9$	$.010_o$

table (4.6)

the symbol r_c' means r_s' in the case of Bardeen's model

EMPIRICAL PSEUDOPOTENTIALS

ELEMENT \ MODEL		$(1+\alpha Q^2+\beta Q^4)\frac{\sin\gamma Q}{\gamma Q}$	$\frac{1+\alpha Q^2+\beta Q^4}{1+\gamma Q^6}$
Na	α'	.324	-.764
	β'	$.061_4$	.766
	γ'	2.541	$.068_8$
	d	$.010_3$	$.005_1$
K	α'	.290	-.902
	β'	$-.025_7$	.130
	γ'	2.678	$.031_8$
	d	$.006_4$	$.005_4$
Rb	α'	.284	-.925
	β'	$-.044_5$	.152
	γ'	2.680	$.028_3$
	d	$.007_9$	$.008_7$

table (4.7)

the calculations were carried out with the EC term

$E_3 = -\frac{1}{2}\frac{X}{1+X}$ for the empirical pseudopotentials

ble ones, thus the results for the EC term $E_1 = -\beta T(1) f(u)$ are not given, since the parameter x_o converged to unreasonable values.

The number d appearing in the tables is the root mean square of the frequency deviations

$$d = \sqrt{\sum_i (\omega_{exp,i} - \omega_i)^2 / N'}$$

where N' is the number of experimental points used for the least squares fit (approximately 35 points in each case).

Some of the calculated dispersion curves (for Na, K and Rb) are plotted in figs.(4.9) to (4.15). Some of the form factors (for the model and empirical pseudopotentials) are plotted along with the experimental ones in figs.(4.16) to (4.18). All the above curves are plotted for the EC term $E_3 = -\frac{1}{2}\frac{\chi}{1+\chi}$. Some of the constants used in the calculations are listed in table (4.8), they are

the Fermi wave vector k_F

the lattice constant a

the constant $\beta = 2/\pi a_o k_F$, a_o is the Bohr radius

the constant $B_o = k_F a/\pi$, B_o occurs when we use the relation

$$u = Q/2k_F$$
$$= \bar{Q}(\pi/ak_F)$$
$$= \bar{Q}/B_o$$

The experimental points for sodium are due to Woods et al (W62), for potassium due to Cowley et al (C66), and for rubidium due to Copley et al (C68).

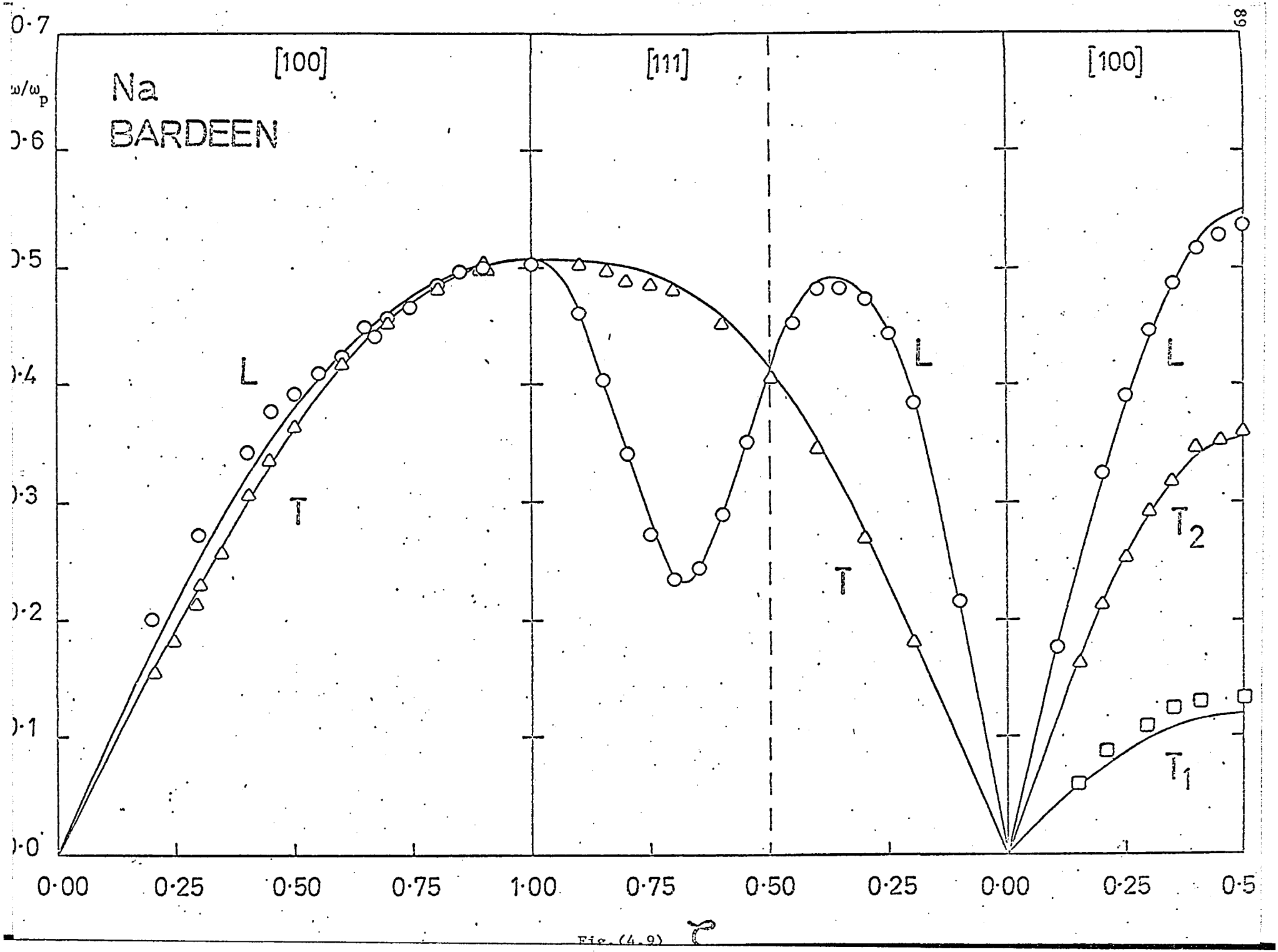

Na
BARDEEN
[100]
[111]
[100]
L
T
L
T
L
T2
T1
ω/ωp
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5

Fig.(4.9)

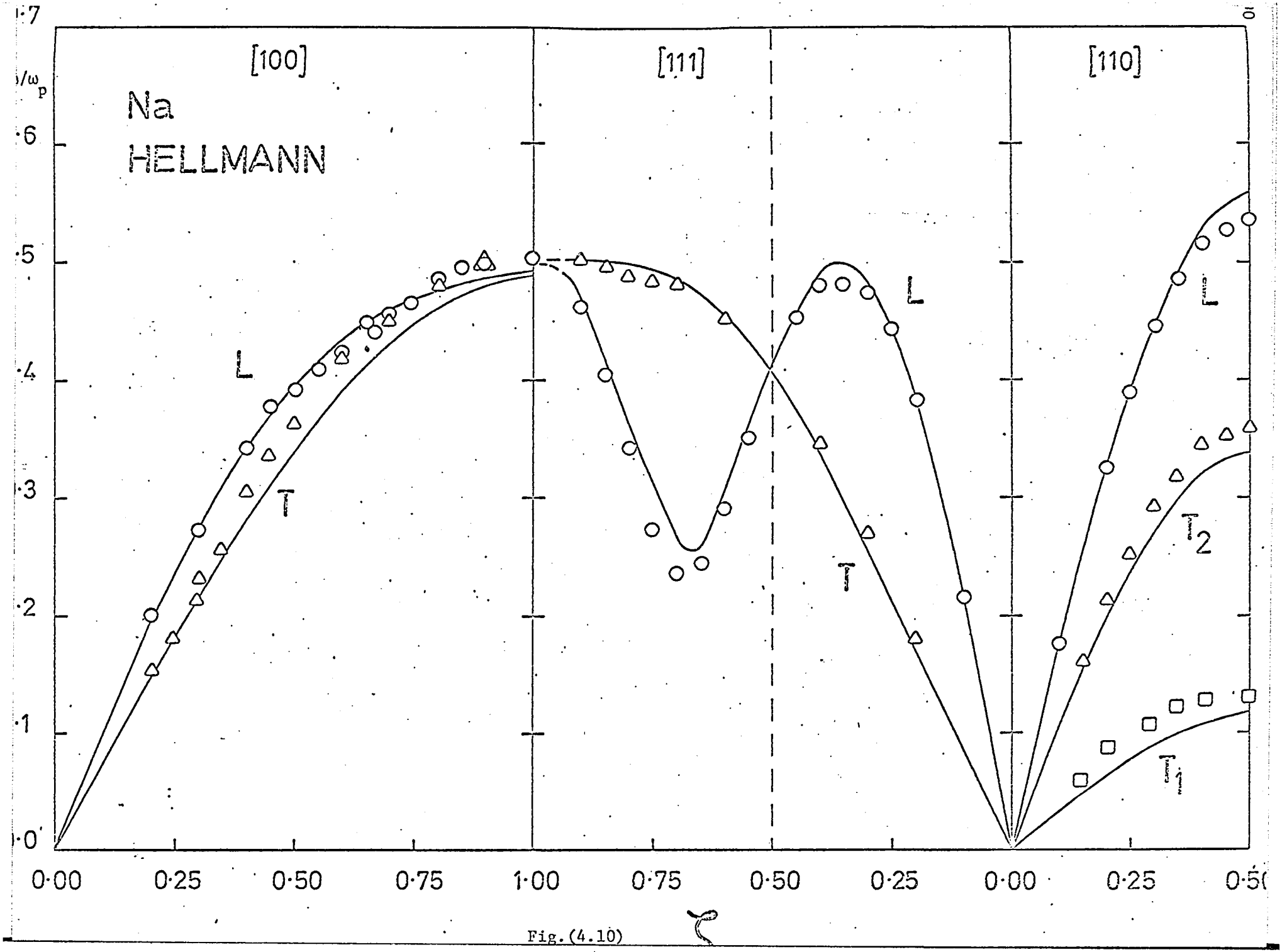

[100]
[111]
[110]
Na
HELLMANN
L
T
L
T
L
T2
T1
ω/ωp
·7
·6
·5
·4
·3
·2
·1
·0
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5
ζ

Fig.(4.10)

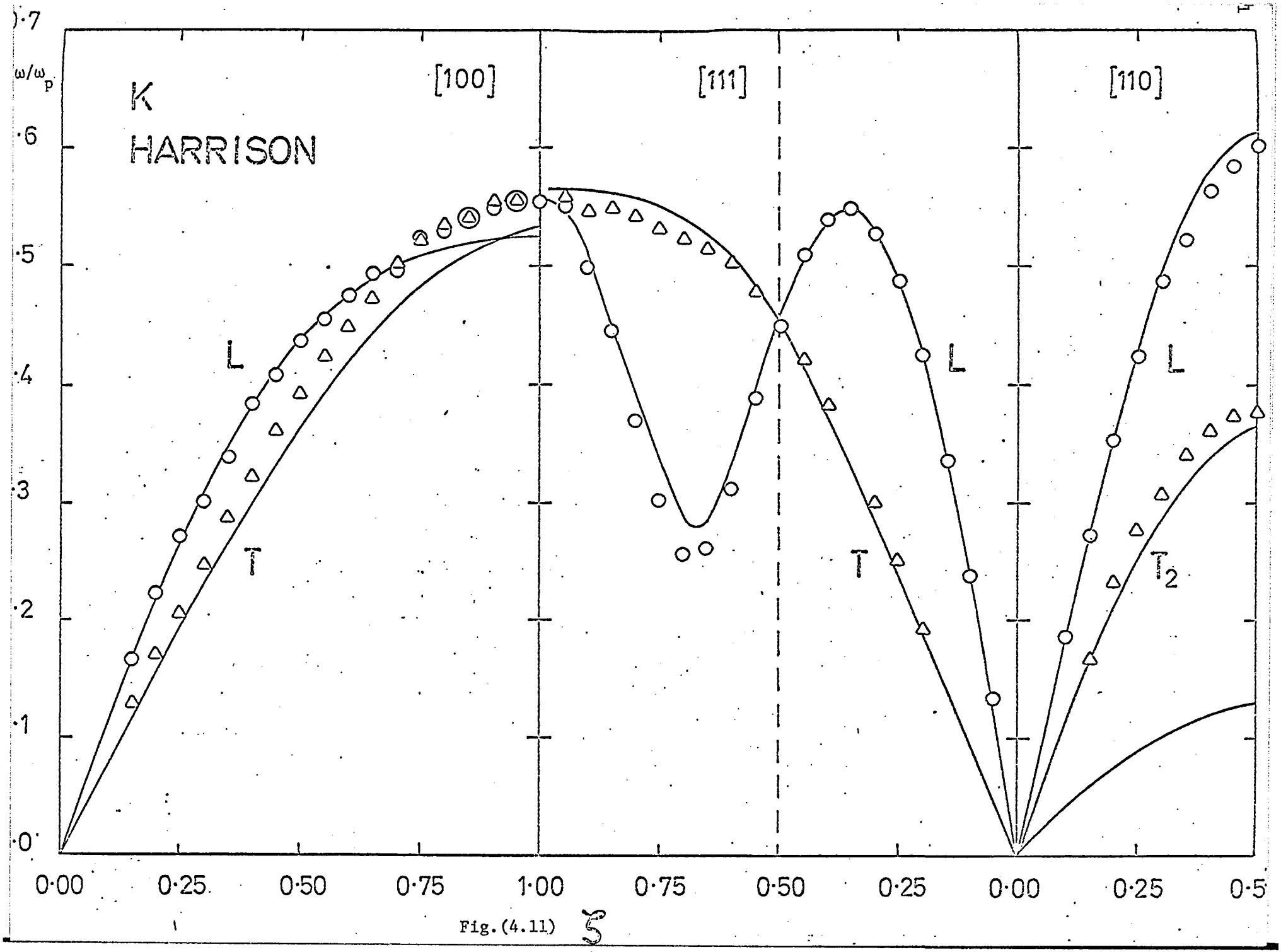

K
HARRISON
[100]
[111]
[110]
ω/ω_p
·7
·6
·5
·4
·3
·2
·1
·0
L
T
L
T
L
T2
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5
ξ

Fig.(4.11)

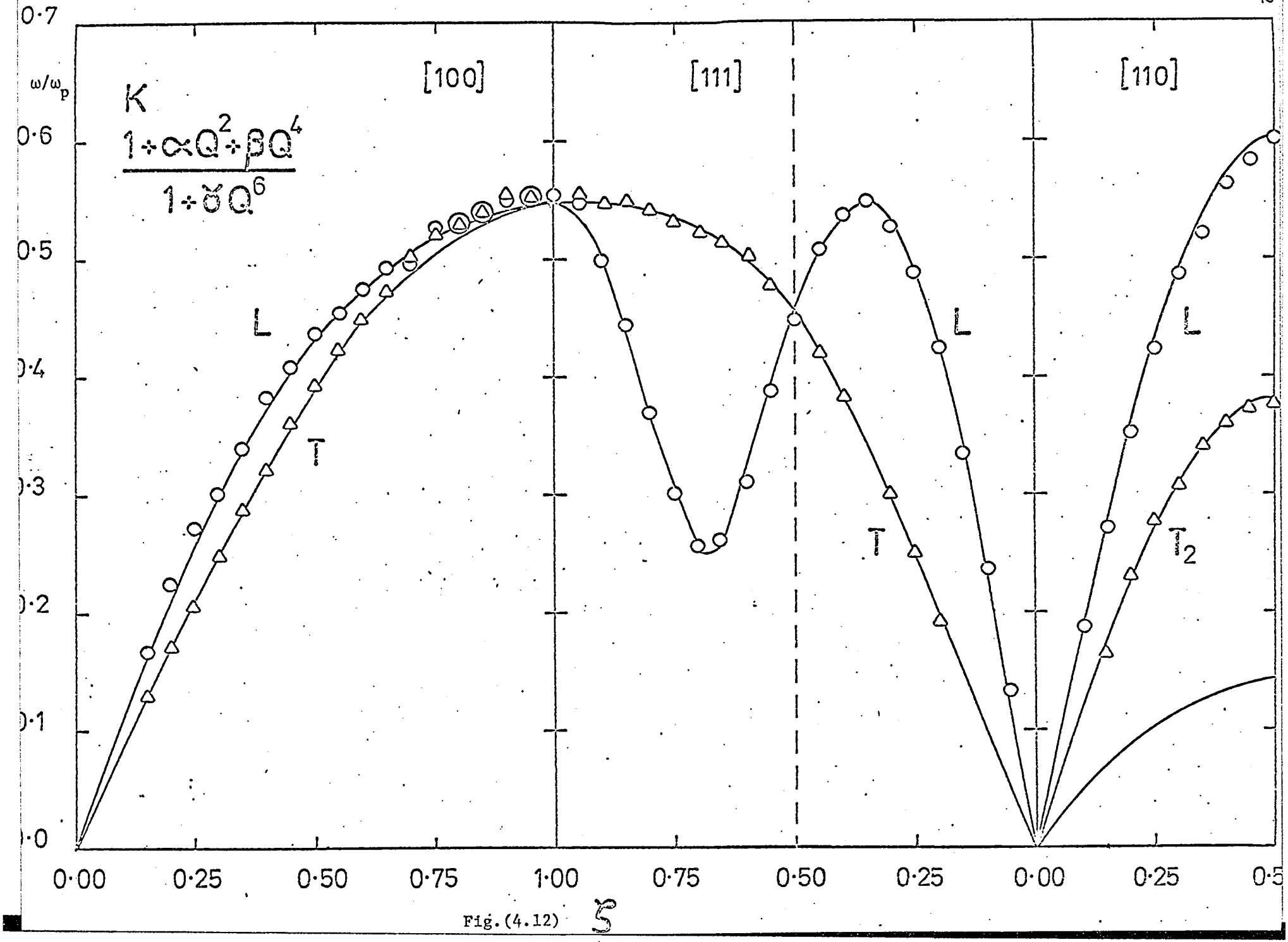

ω/ω_p
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
K
1+αQ²+βQ⁴
1+γQ⁶
[100]
[111]
[110]
L
T
L
T
L
T
T₂
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5
ζ

Fig.(4.12)

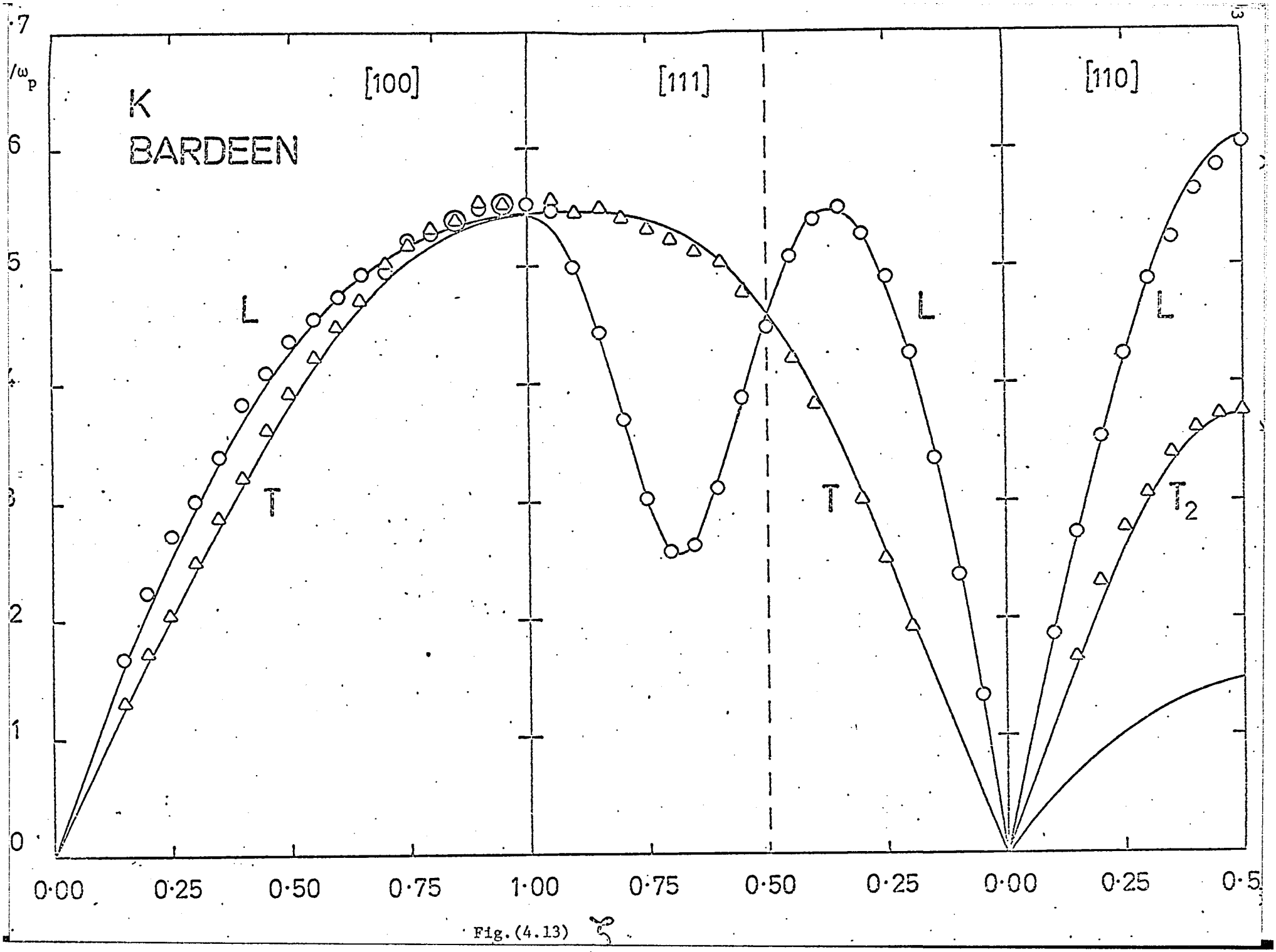

K
BARDEEN
[100]
[111]
[110]
L
T
L
T
L
T2
/ωp
7
6
5
2
1
0
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5

Fig.(4.13)

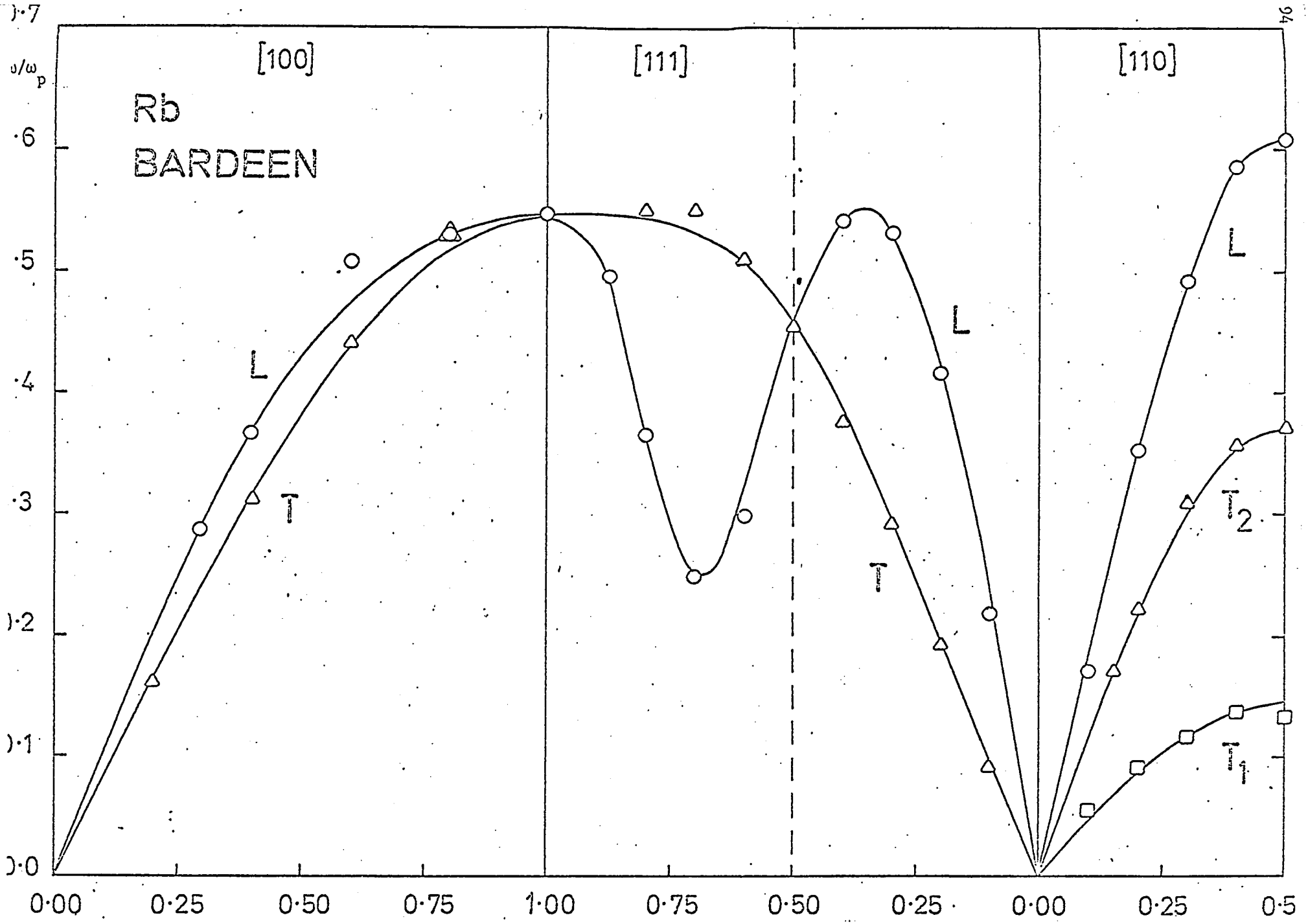

[100]
[111]
[110]
Rb
BARDEEN
ω/ω_p
·7
·6
·5
·4
·3
·2
·1
·0
L
T
L
T
L
T2
T1
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5
ζ

Fig. (4.14)

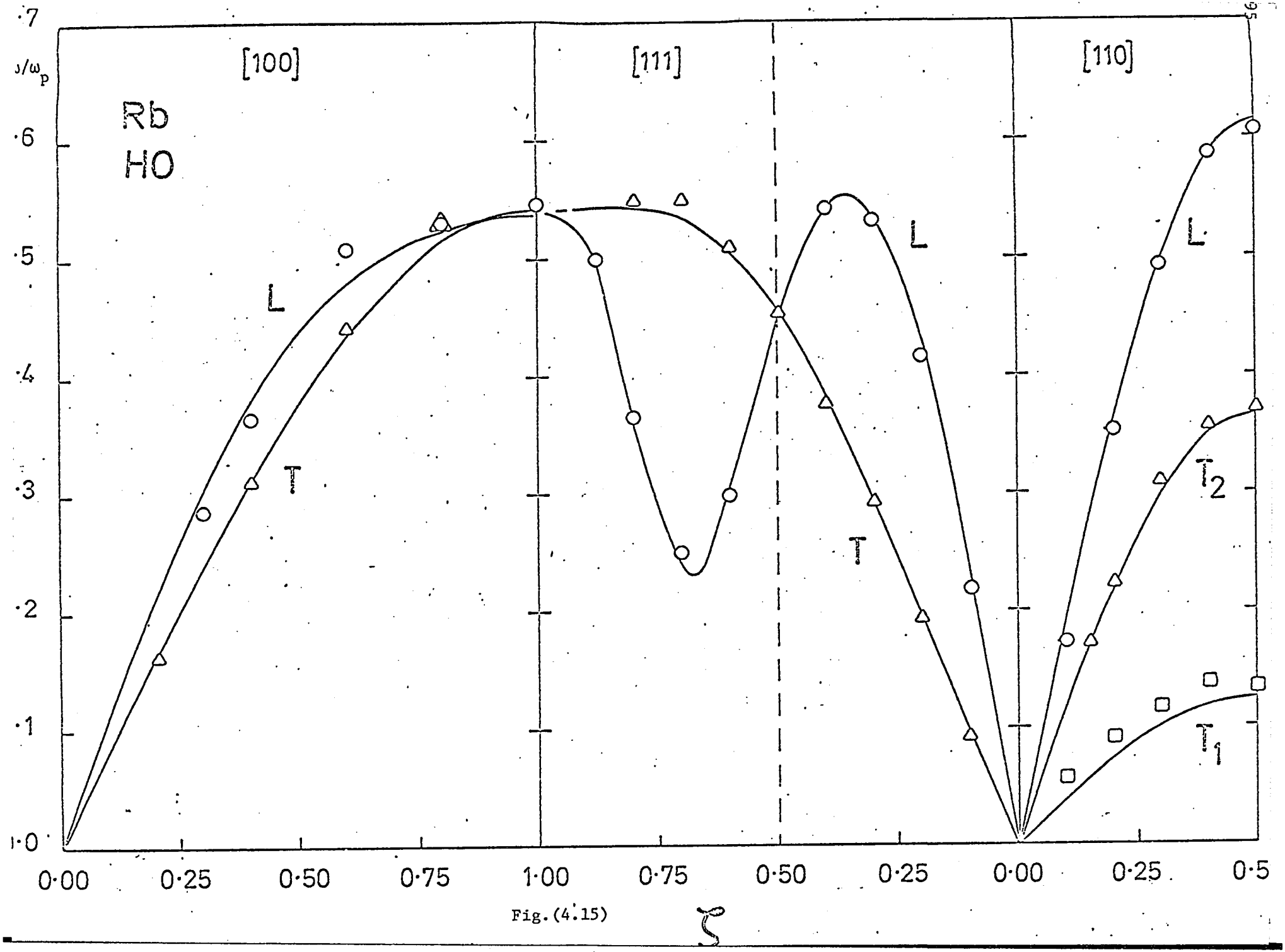

[100]
[111]
[110]
Rb
HO
L
T
L
T
L
T2
T1
ω/ωp
·7
·6
·5
·4
·3
·2
·1
1·0
0·00
0·25
0·50
0·75
1·00
0·75
0·50
0·25
0·00
0·25
0·5
ζ

Fig. (4.15)

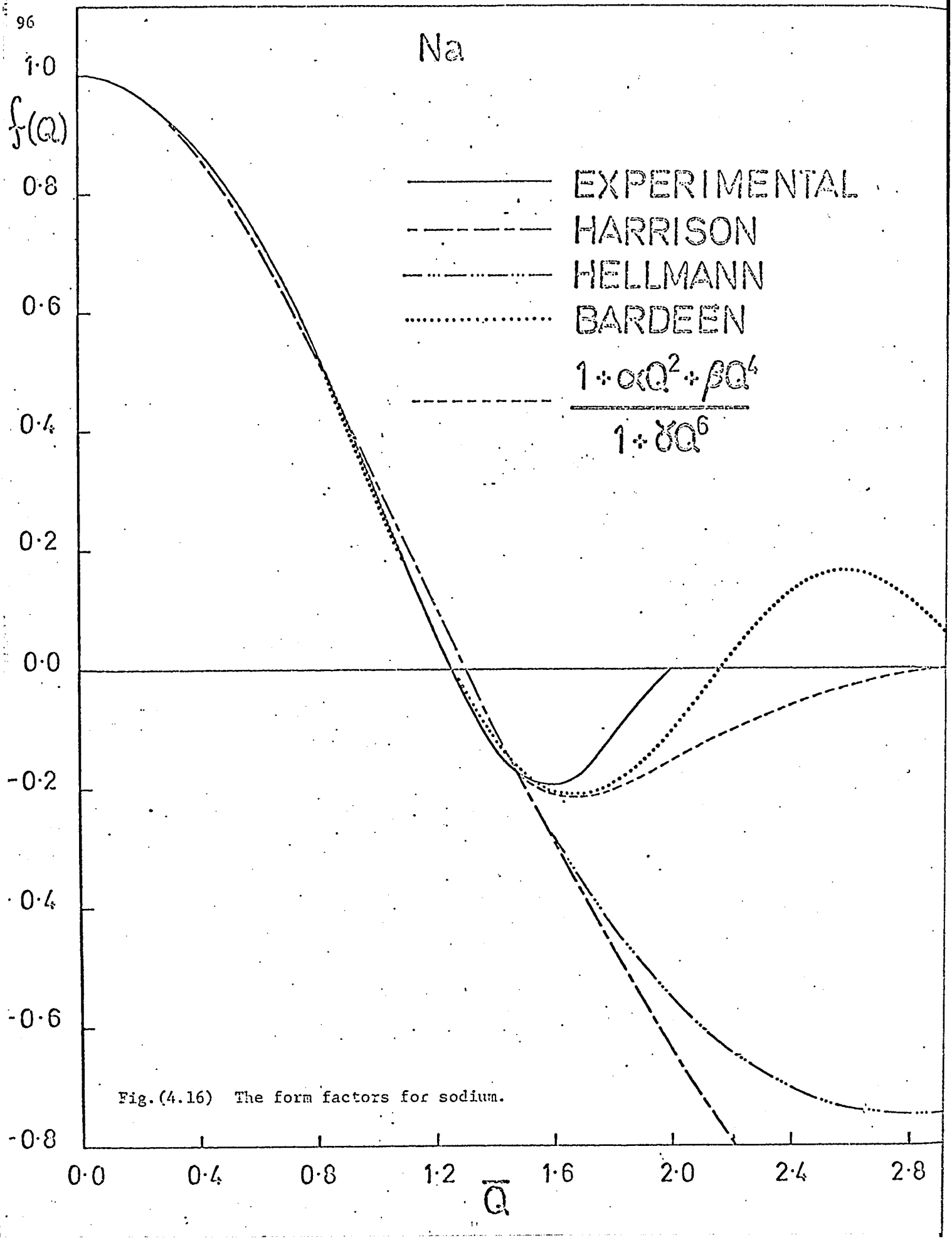


Fig.(4.16) The form factors for sodium.

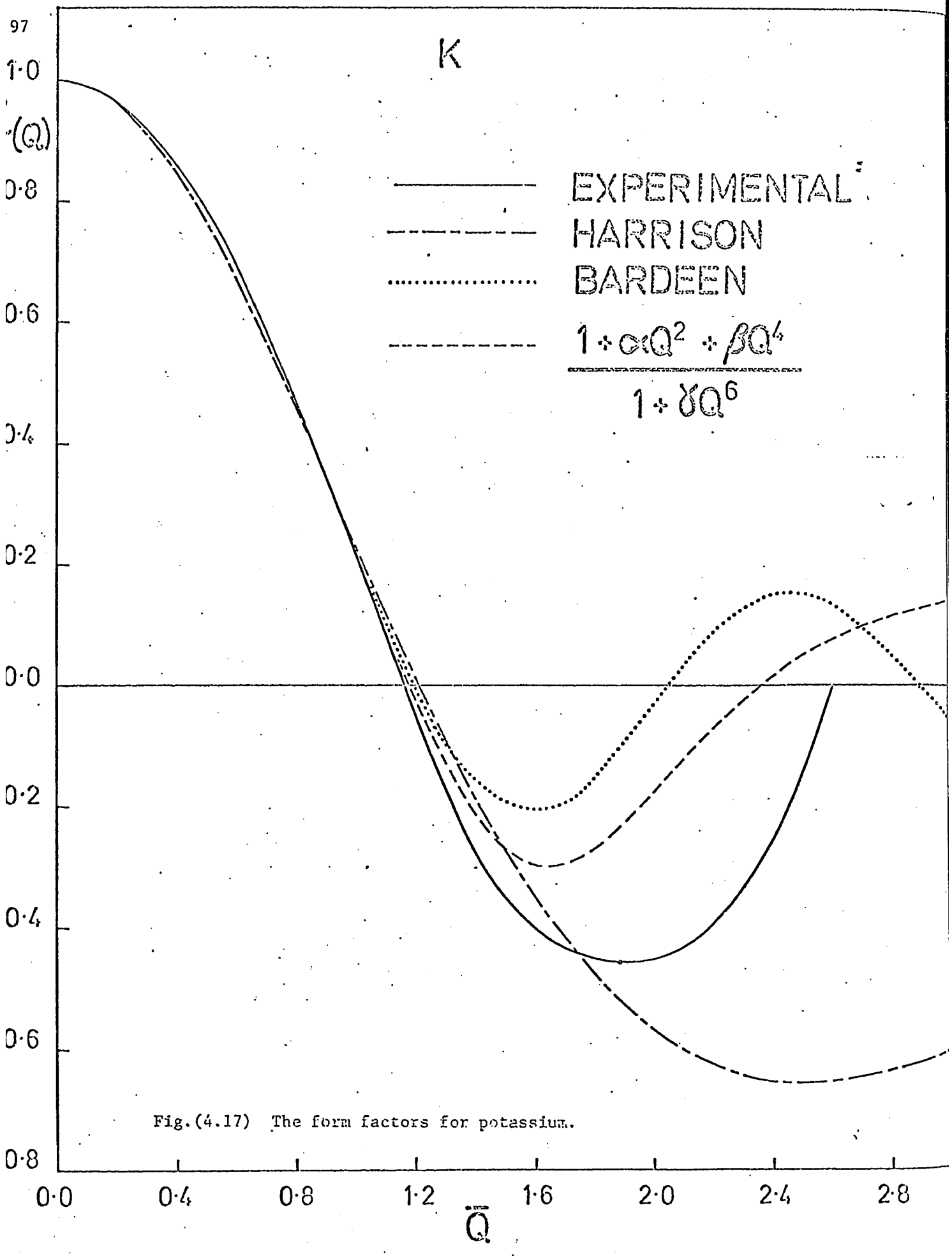


Fig.(4.17) The form factors for potassium.

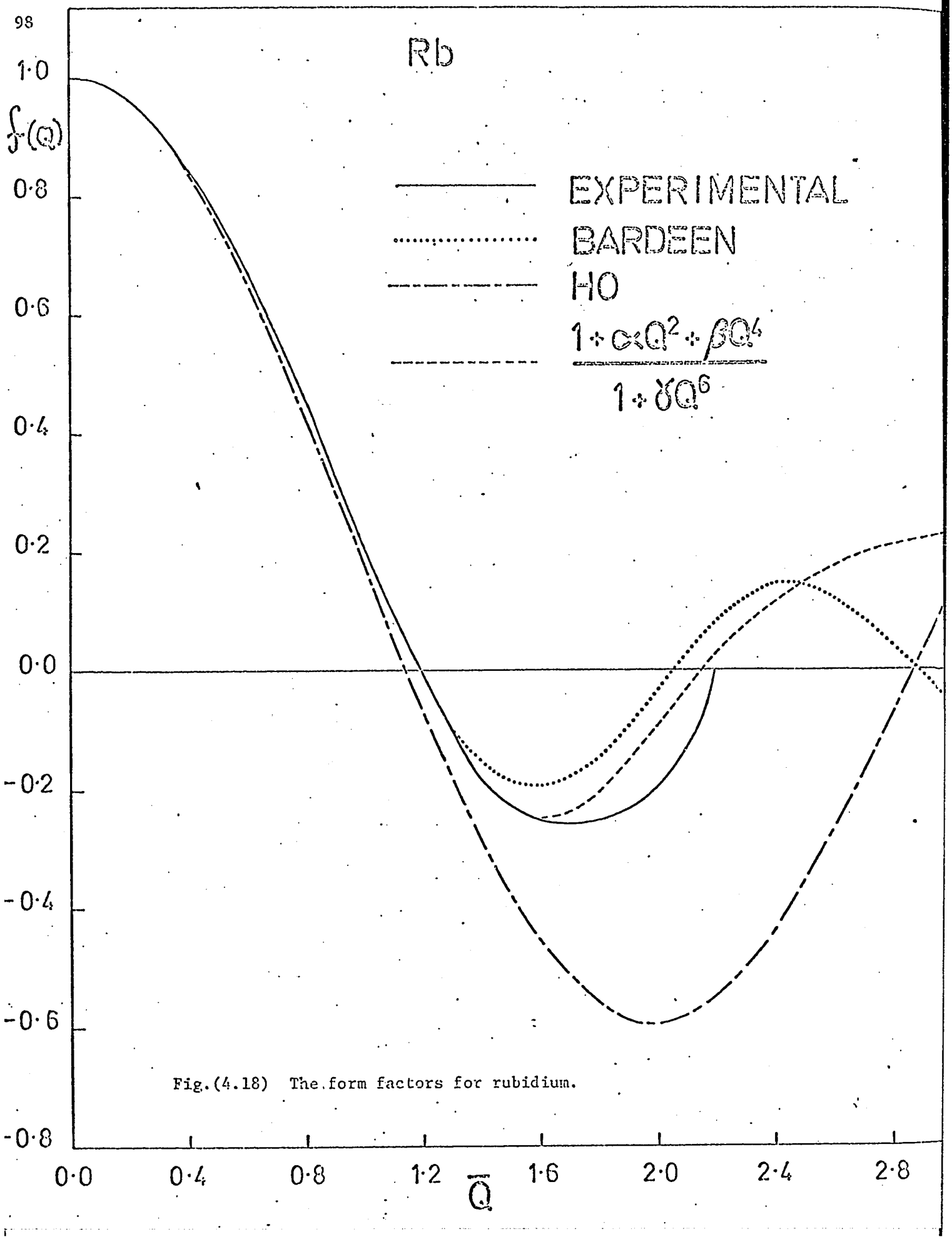


Fig.(4.18) The form factors for rubidium.

	$k_F \times 10^{-8}$ cm^{-1} *	Temp ^oK	a A^o	β	B_o
Na	.90	90	4.237[a]	1.337	1.214
K	.73	9	5.225[b]	1.648	1.214
Rb	.68	120	5.628[c]	1.770	1.218

table (4.8)

*ref. K66

a ref. (G63)
b ref. (P58)
c ref. (C68)

5. The Interatomic Potentials

As mentioned previously the potential between two atoms can be divided into two parts: the Coulomb potential V_c and the electronic contribution V_E. When the electronic contribution is subtracted from the Coulomb potential, it leaves a comparatively small interatomic potential V. Writing this in terms of the Fourier transforms we get

$$V(Q) = V_c(Q) - V_E(Q)$$

$$= \frac{4\pi e^2}{vQ^2} - V_E(Q)$$

Thus

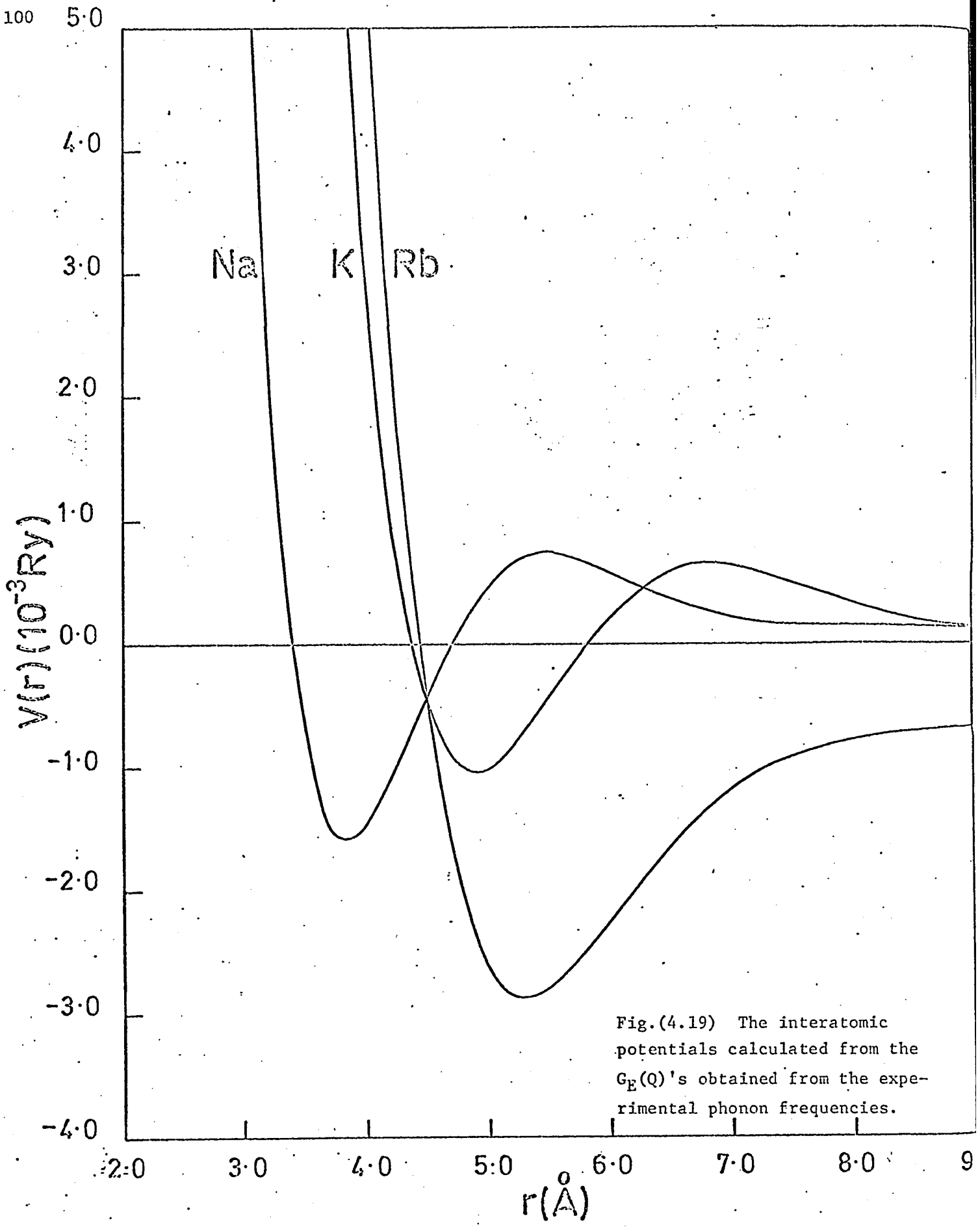


Fig.(4.19) The interatomic potentials calculated from the $G_E(Q)$'s obtained from the experimental phonon frequencies.

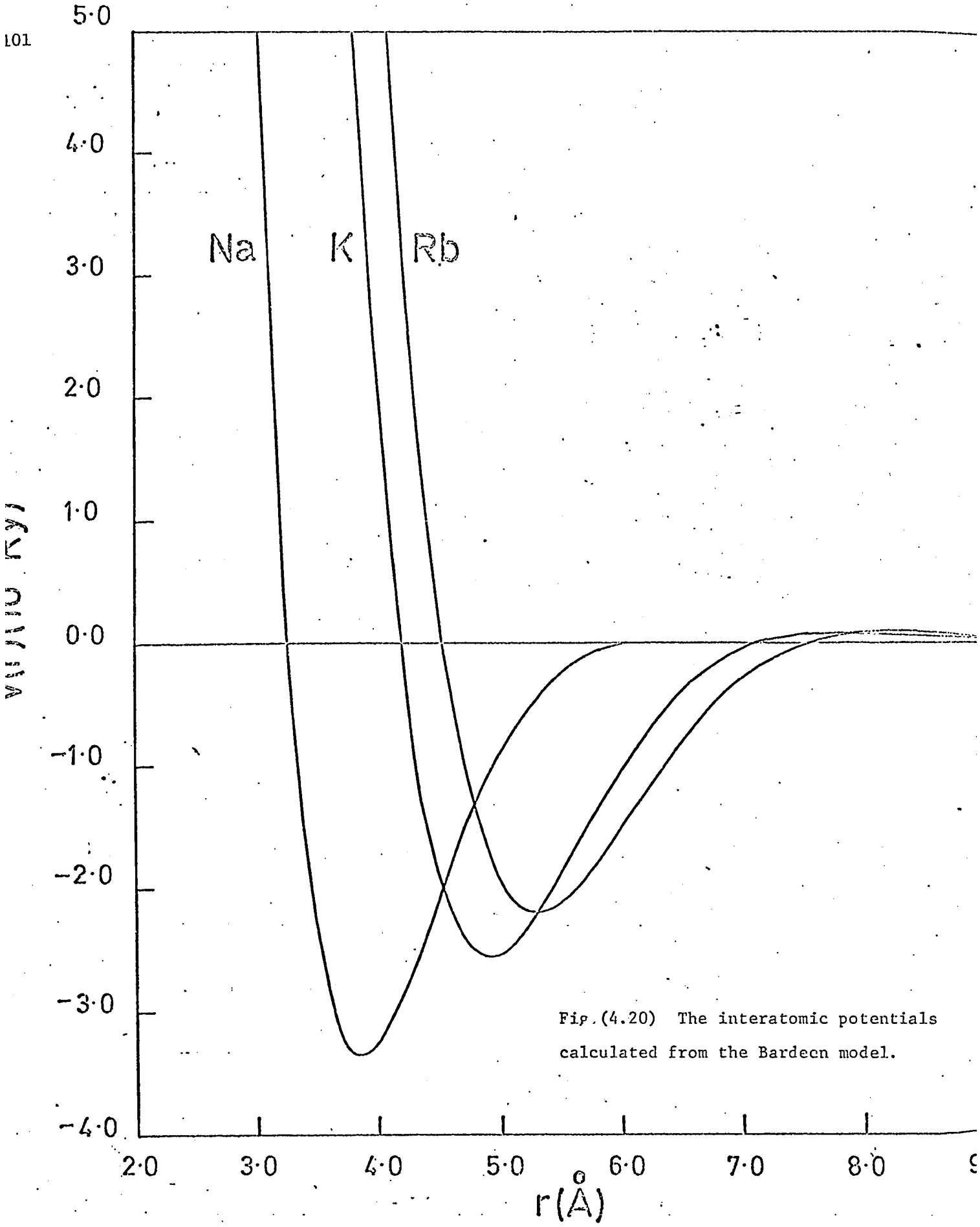


Fig.(4.20) The interatomic potentials calculated from the Bardeen model.

$$V(r) = \frac{e^2}{r} - \frac{v}{(2\pi)^3}\int V_E(Q)\exp(i\vec{Q}\cdot\vec{r})d^3Q$$

$$= \frac{e^2}{r} - \frac{2e^2}{\pi}\int_0^\infty G_E(Q)\,\frac{\sin Qr}{Qr}\,dQ$$

where we have used

$$V_E(Q) = \frac{4\pi e^2}{vQ^2}\,G_E(Q)$$

Thus a knowledge of $G_E(Q)$ gives us the interatomic potentials. These were computed using the $G_E(Q)$'s of table (4.3) obtained from the experimental phonon dispersion curves. The results for Na, K and Rb are shown in fig.(4.19). The Bardeen model was also used, the results (using the parameters obtained from the least squares fit) are shown in fig.(4.20). The above results were computed using the EC term $E_3 = -\frac{1}{2}\frac{\chi}{1+\chi}$.

6. Discussion of the Results

To study the role of the exchange and correlation (EC) term we must see to what extent it affects the function

$$\Lambda(Q) = \frac{\chi(Q)}{\epsilon_{el}(Q)}$$

which enters the lattice dynamics through the equation

$$G_E(Q) = f^2(Q)\Lambda(Q)$$

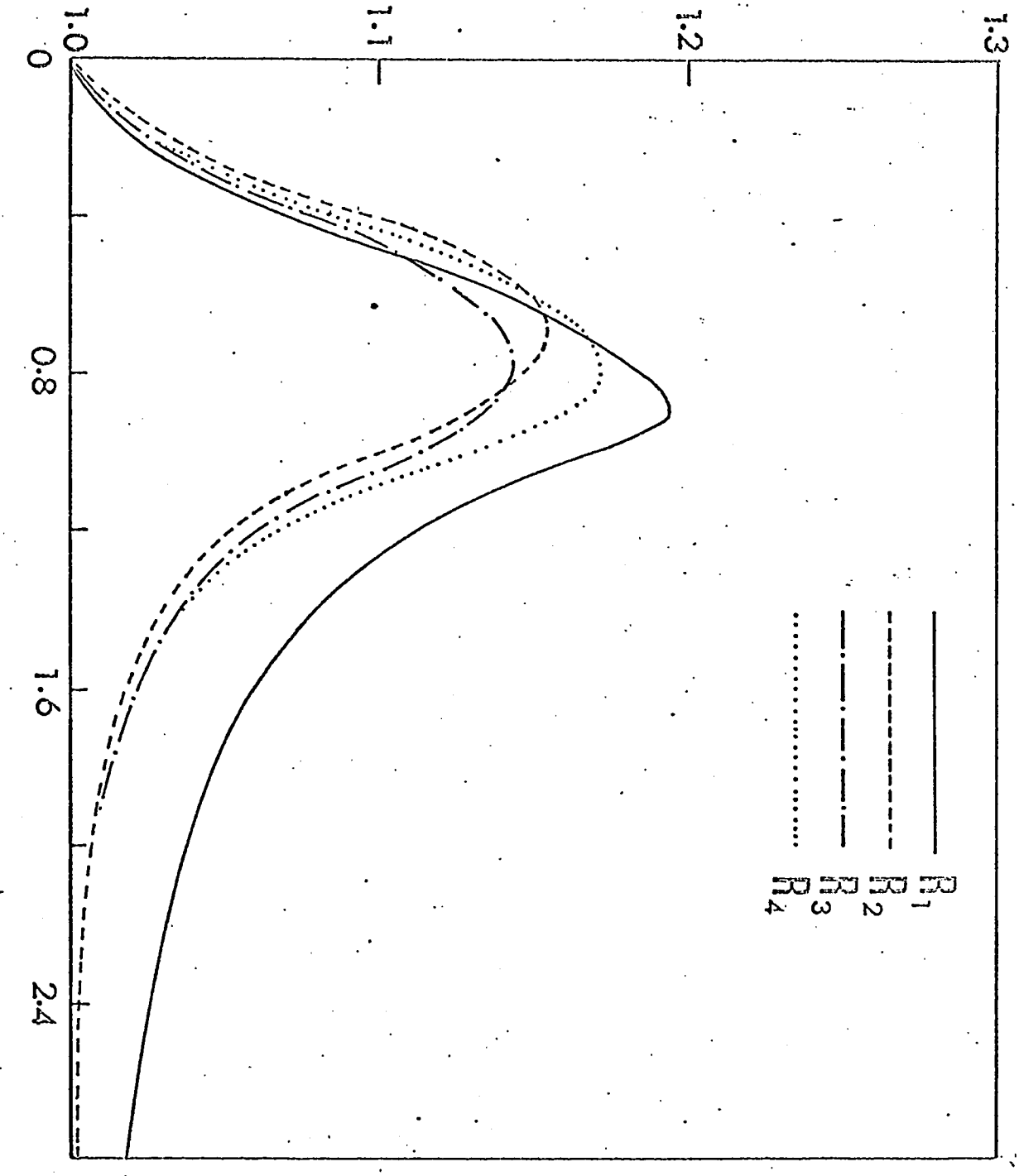


Fig.(4.21) The ratios $R_i = \Lambda_i / \Lambda_{Hartree}$

To see this we plot the ratios

$$R_i = \Lambda_i / \Lambda_{Hartree} \qquad i = 1, \ldots, 4$$

where Λ_i contains the EC term E_i defined in sec.4 of this chapter, and $\Lambda_{Hartree}$ is the same function in the Hartree approximation, that is, without exchange and correlation.

The ratios are plotted in fig.(4.21). We see that R_1 for the EC term $E_1 = -\beta T(1) f(u)$ is not in the class of R_2, R_3 and R_4, because it falls to zero much more slowly. This is probably why the EC term E_1 did not yield acceptable results for the non-linear least squares fit; the parameter x_o converged to physically unreasonable values in most cases.

We now discuss the results for the model pseudopotentials. When we scan tables (4.4), (4.5) and (4.6), comparing the root mean square of the frequency deviations and when we examine the dispersion curves plotted in figs.(4.9) to (4.15), we see that, of the four model potentials of section 3, the Bardeen model gives the best results. The agreement with experiment is good for all branches, for Na, K and Rb with the exception of the T_1 branch in the [1,1,0] direction for Na, and the narrow separation of the L and T branches in the [1,0,0] direction for Na.

The degeneracy at $q = q_{max}$ for the [1,0,0] direction is lacking for the dispersion curves obtained from the Harrison and Hellmann models. This is due to the prominent tail in the form factors for these two models, in contrast to the relatively smaller tail for the experimentally derived form factors. Fig.(4.16) shows this feature clearly. The prominent tail of the Harrison and Hellmann models extends to relatively large values of

$\bar{Q}$, thus requiring a relatively larger number of reciprocal lattice points in the summation as compared to the other potentials. Eighty-seven points were used in our work and we did not consider it worthwhile to increase the number of points in view of the poor results from the Harrison and Hellmann models for the form factors (Figs.(4.16), (4.17) and (4.18)). Harrison (H66) in an application of his model to Aluminium also obtained curves without degeneracies at the points where they were expected. When examining the form factors we also see why the Bardeen model gives better results than the other model potentials; its form factor stays closer to the experimentally derived one over the whole range. Figs.(4.16), (4.17) and (4.18) depict this clearly.

Examining tables (4.4) to (4.6) we also note that there is no advantage in having the extra parameter x_o in the EC term $E_2 = \frac{-\beta f(u)}{4u^2 + x_o^2}$ since the root mean squares of the frequency deviations are not smaller than those for the other EC terms.

For the empirical form factors, the best results were obtained with $f_2(Q) = \frac{1 + \alpha Q^2 + \beta Q^4}{1 + \gamma Q^6}$. The dispersion curves plotted for K in fig.(4.12) show that the agreement with the experimental data is excellent (they are even better than the results for the Bardeen pseudopotential). The form factors for this empirical model are very close to the experimentally derived ones for Na, K and Rb. As shown by table (4.7) the root mean square of the deviations are smaller than those of the model pseudopotentials (of section 3) for Na and K. The results for the form factor $f_1(Q) = (1+\alpha Q^2+\beta Q^4)\frac{\sin\gamma Q}{\gamma Q}$ are also shown in table (4.7). All the results for the empirical pseudopotentials were computed with the EC term

$E_3 = -\frac{1}{2}\frac{\chi}{1+\chi}$. No results for the form factors $f_3(Q) = \frac{1+\alpha Q^2+\beta Q^4+\gamma Q^6}{1+\gamma Q^8}$ and $f_4(Q) = (1+\alpha Q^2+\beta Q^4)g(\gamma Q)$ are given because the parameters usually diverged. Other expressions were also tried, but the most useful one was found to be $f_2(Q)$ as mentioned above.

We now discuss the interatomic potentials. Fig.(4.19) shows the potentials computed for Na, K and Rb using the $G_E(Q)$'s obtained from the experimental phonon frequencies. The potential computed for Rb is not similar to those for Na and K. This is probably due to a difference in the shape of the experimentally derived form factors. The potential obtained for K is similar to that of Cowley et al (C66). The interatomic potentials computed from the Bardeen model are shown in fig.(4.20). They are similar to those obtained by Ho (H68). This terminates the discussion of the systematic study of the pseudopotentials, made with various expressions for the exchange and correlation term.

Appendix A. Integration of Bailyn's Equation for $\varepsilon_{el}(Q)$

The equation under consideration is

$$\varepsilon_{el}(Q) = 1 + 4\pi e^2 \sum_{k'} \left(\frac{4}{Q^2} - \frac{3h(x)}{k_F^2} - \frac{3h(x')}{k_F^2} \right) \frac{n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad \text{(A1)}$$

We have two integrations to perform: one involving h(x) and one involving h(x').

First integration (involving h(x)): Fig.(a1) shows us the range of integration as defined by the boundary of the sphere $n(\vec{k}')$. The variables ϕ, Θ and k' are defined as shown. Their limits are

$$\begin{cases} \phi : 0 \to 2\pi \\ \Theta : 0 \to \pi \\ k' : 0 \to k_F \end{cases}$$

Thus for the first integration

$$\sum_{k'} \equiv \frac{1}{(2\pi)^3} \int d^3\vec{k}'$$

$$= \frac{1}{(2\pi)^3} \int_0^{2\pi} d\phi \int_0^{\pi} \cos\Theta \, d\Theta \int_0^{k_F} k'^2 dk'$$

$$= \frac{k_F^3}{4\pi^2} \int_0^1 x^2 dx \int_{-1}^{+1} d\mu \qquad \text{(A2)}$$

where $x = k'/k_F$ and $\mu = \cos\Theta$

Second integration (involving h(x')) There are two cases: the case $Q < k_F$ i.e. $u < .5$ and the case $Q > k_F$ i.e. $u > .5$.

Case $u < .5$ We first apply the transformation $\vec{k}'' = \vec{k}' - \vec{Q}$ to the energy denominator of eq.(A1). This amounts to moving the origin from O' to O'' in fig.(a2). We choose $\vec{Q}$ along the z axis. The integration falls into two parts:

i) the smaller sphere of radius k_F-Q defined by $\begin{cases} \phi : 0 \to 2\pi \\ \Theta : 0 \to \pi \\ k'' : 0 \to k_F - Q \end{cases}$

and ii) the crescent shaped portion defined by $\begin{cases} \phi : 0 \to 2\pi \\ \Theta : \Theta_c \to \pi \\ k'' : k_F - Q \to k_F + Q \end{cases}$

where Θ_c is the lower limit of integration for Θ and is defined in fig.(a3). (We get the same equation for Θ_c for the case $u < .5$ and $u > .5$). Using these limits we obtain

$$\sum_{\vec{k}'} = \frac{k_F^3}{4\pi}\left[\int_0^{1-2u} x^2dx\int_{-1}^{+1} d\mu + \int_{1-2u}^{1+2u} x^2dx\int_{-1}^{\mu_c} d\mu\right] \qquad \text{(A3)}$$

Case $u > .5$ The limits of integration are depicted in fig.(a3), and are $\begin{cases} \phi : 0 \to 2\pi \\ \Theta : \Theta_c \to \pi \\ k'' : Q - k_F \to Q + k_F \end{cases}$

so we get for this case

$$\sum_{k'} = \frac{k_F^3}{4\pi^2} \int_{2u-1}^{2u+1} x^2 dx \int_{-1}^{\mu_c} d\mu \qquad \text{(A4)}$$

We now use these results to perform the integration. We give the details for the case u < .5. Using eq.(A2) for the term involving h(x) and eq. (A3) for the term involving h(x') we obtain from eq.(A1)

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u}\left[\int_0^1 3h(x)x \ln g_o \, dx - \int_0^{1-2u} 3h(x)x \ln g_o \, dx - \int_{1-2u}^{1+2u} 3h(x)x \ln g_- \, dx\right] \qquad \text{(A5)}$$

where $g_o = \left|\frac{x+u}{x-u}\right|$ and $g_\pm = \left|\frac{4u(x \pm u)}{1-x^2}\right|$

Combining these integrals into one we obtain

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u} \int_{1-2u}^{1+2u} 3h(x)x \ln g \, dx \qquad \text{(A6)}$$

where $g = \begin{cases} g_+ & \text{for } x < 1 \\ g_- & \text{for } x > 1 \end{cases}$

When the case u < .5 and the case u > .5 are combined we obtain

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u} \int_{y_o}^{1+2u} 3h(x)xQ(x,u)dx$$

which is eq.(2.29), y_o and Q(x,u) are defined as in eq.(2.29).

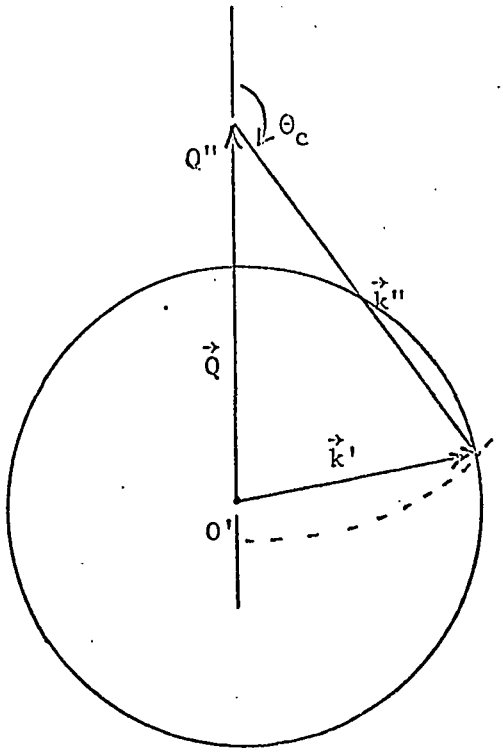


fig.(a3)

We know that $\vec{k}'' = \vec{k}' - \vec{Q}$

so $\vec{k}' = \vec{k}'' + \vec{Q}$

and $k'^2 = k''^2 + Q^2 + 2k''Q \cos \Theta$

where Θ is the angle between $\vec{Q}$ and $\vec{k}''$, it has the lower limit $\Theta = \Theta_c$.

So substituting this back into the equation we get

$$k_F^2 = k''^2 + Q^2 + 2k''Q \cos \Theta_c$$

Let $x = k''/k_F$, $u = Q/2k_F$, $\mu_c = \cos \Theta_c$, we solve for μ_c to obtain

$$\mu_c = (1 - x^2 - 4u^2)/4ux$$

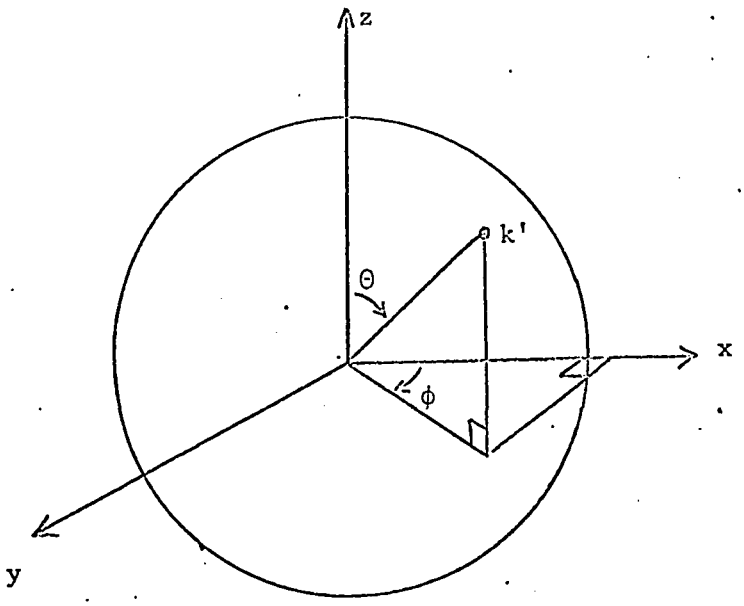


fig.(a1)

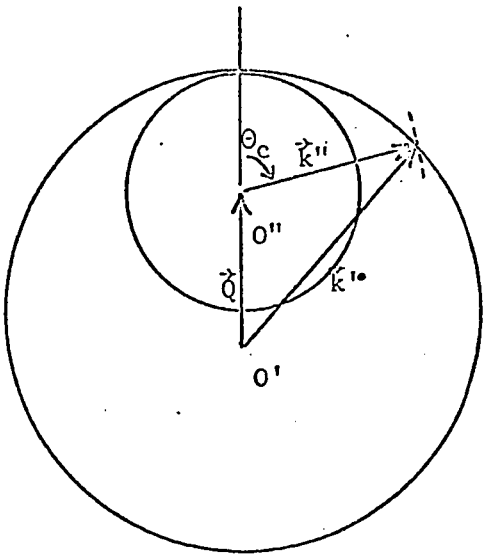


fig.(a2)

Appendix B. Correction for some Results in Hone's Work

Hone makes a mistake in the determination of μ_c and this affects the subsequent integrals.

He gives the expression $$\mu_c = \frac{x^2 - v^2 - 1}{2v} \qquad \text{(B1)}$$

while the correct expression is $$\mu_c = \frac{1 - v^2 - x^2}{2vx} \qquad \text{(B2)}$$

where $x = k''/k_F$ and $v = Q/k_F$.

The proof that eq.(B2) is correct can be given as follows. The volume enclosed by the big sphere of fig.(a2) is $\frac{4\pi k_F^3}{3}$ and is made of two parts: the little sphere and the crescent shaped portion. The integral for the total volume is given by eq.(A3), which we write

$$\int d^3\vec{k}'' = 2\pi k_F^3 \left[\int_0^{1-v} x^2 dx(2) + \int_{1-v}^{1+v} x^2 dx(\mu_c + 1) \right] \qquad \text{(B3)}$$

The two parts of the volume are written separately. When integrated (using the proper value of μ_c) eq.(B3) should yield

$$\int d^3\vec{k}'' = \frac{4\pi k_F^3}{3}$$

Substituting Hone's μ_c into eq.(B3) we get

$$\int d^3\vec{k}'' = 2\pi k_F^3 \left[\frac{2}{3}(1-v)^3 + \frac{(v+1)^2}{6v}\left\{(1+v)^3 - (1-v)^3\right\} - \frac{1}{10v}\left\{(1+v)^5 - (1-v)^5\right\} \right] =$$

$$= 2\pi k_F^3 \left[\ \ldots \ \frac{v^4}{3} - \frac{v^4}{5} \ \ldots \ \right]$$

We see that the higher power terms (for example the terms in v^4) do not cancel and we do not obtain $\frac{4\pi k_F^3}{3}$.

Now substituting our value of μ_c as given by eq.(B2) we get

$$\int d^3\vec{k}'' = 2\pi k_F^3 \left[\frac{2}{3}(1-v)^3 + \frac{1}{3}\left\{(1+v)^3 - (1-v)^3\right\} - \frac{1}{8v}\left\{(1+v)^4 - (1-v)^4\right\} - \frac{(v^2-1)}{4v}\left\{(1+v)^2 - (1-v)^2\right\}\right]$$

$$= 2\pi k_F^3 \left[\frac{2}{3} - 2v + 2v^2 - \frac{2}{3}v^3 + 2v + \frac{2}{3}v^3 - 1 - v^2 - v^2 + 1 \right]$$

$$= \frac{4\pi k_F^3}{3}$$

which is the correct result.

Appendix C. Integration of the Equation for $\varepsilon_{el}(Q)$

Our starting point is eq.(2.44) which we write

$$\varepsilon_{el}(Q) = 1 - \frac{8\pi e^2}{Q^2}\sum_{k'}\left(1 - 2u^2AV(x)\right)\frac{n(\vec{k}'-\vec{Q}) - n(\vec{k}')}{E_{k'-Q} - E_{k'}} \qquad (C1)$$

There are two cases: the case u < .5 and the case u > .5. We shall treat the case u < .5. The factor $n(\vec{k}'-\vec{Q}) - n(\vec{k}')$ determines the range of integration; it is the hatched portion shown in fig.(c1). The term $-n(\vec{k}')$ gives a minus sign in front of the integral which is over the lower crescent.

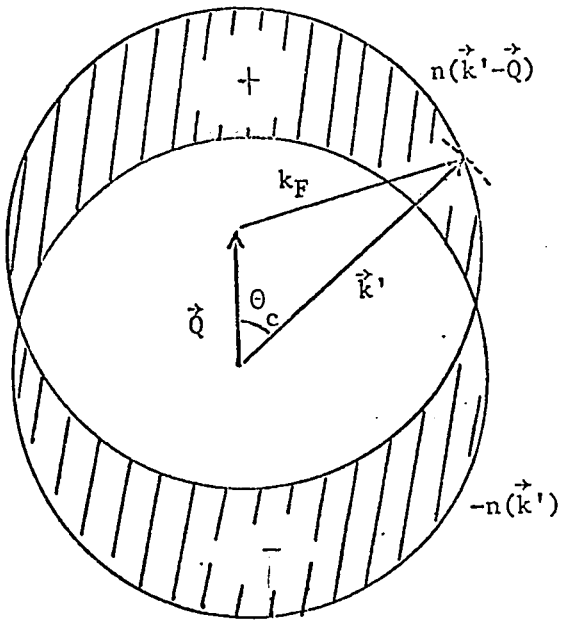


fig.(c1)

So we have

$$\sum_{k'} \equiv \frac{1}{(2\pi)^3}\int d^3\vec{k}' = \frac{1}{4\pi^2}\left[-\int_{k_F-Q}^{k_F} k'^2dk' \int_{\theta_c}^{\pi} \sin\theta\, d\theta + \int_{k_F}^{k_F+Q} k'^2dk' \int_{o}^{\theta_c} \sin\theta\, d\theta\right] \qquad (C2)$$

Θ_c is a limit of integration for the angle Θ and is found as follows: in the triangle shown in fig.(c1) we have

$$k_F^2 = Q^2 + k'^2 - 2Qk'\cos\Theta_c$$

thus $\cos\Theta_c = (Q^2 + k'^2 - k_F^2)/2Qk'$

which we write as $\mu_c = (4u^2 + x^2 - 1)/4ux$

where $\mu_c = \cos\Theta_c$, $u = Q/2k_F$, $x = k'/k_F$.

In terms of the variables x, u and μ eq.(C2) becomes

$$\sum_{k'} \equiv \frac{k_F^3}{4\pi^2}\left[\int_{1-2u}^{1} x^2dx\int_{\mu_c}^{-1} d\mu + \int_{1}^{1+2u} x^2dx\int_{\mu_c}^{1} d\mu\right] \qquad (C3)$$

We shall take the energy $E_{k'}$ in the parabolic band approximation thus

$$E_{k'} = \frac{\hbar^2}{2m'}k'^2 = \frac{\hbar^2k_F^2}{2m'}x^2$$

Substituting into eq.(C1) and writing in terms of x, u and μ we get

$$\varepsilon_{el}(Q) = 1 - \frac{\beta\pi^2}{2u^3k_F^3}\sum_{k'}\left(1 - 2u^2AV(x)\right)\frac{n(x-2u) - n(x)}{u - x\mu} \qquad (C4)$$

where $\beta = 2/\pi a_o k_F$. We now use eq.(C3) to get

$$\varepsilon_{el}(Q) = 1 - \frac{\beta}{8u^3}\left[\int_{1-2u}^{1} x^2dx\int_{\mu_c}^{-1} d\mu + \int_{1}^{1+2u} x^2dx\int_{\mu_c}^{1} d\mu\right]\frac{(1-2u^2AV(x))}{u - x\mu}$$

$$= 1 + \frac{\beta}{8u^3}\left[\int_{1-2u}^{1} x\,dx \int_{\mu_c}^{-1} \frac{d(-x\mu)}{u-x\mu} + \int_{1}^{1+2u} x\,dx \int_{\mu_c}^{1} \frac{d(-x\mu)}{u-x\mu}\right](1 - 2u^2 AV(x))$$

$$= 1 + \frac{\beta}{8u^3}\left[\int_{1-2u}^{1} x \ \ell n\left|\frac{4u(u+x)}{1-x^2}\right| + \int_{1}^{1+2u} x \ \ell n\left|\frac{4u(u-x)}{1-x^2}\right|\right](1-2u^2 AV(x))\,dx$$

$$= 1 + \frac{\beta}{8u^3}\int_{1-2u}^{1+2u} x \ \ell n\ g(1 - 2u^2 AV(x))\,dx \qquad \text{(C5)}$$

where $g = \begin{cases} g_+ & \text{for } x < 1 \\ g_- & \text{for } x > 1 \end{cases}$ $\qquad g_\pm = \left|\frac{4u(x \pm u)}{1 - x^2}\right|$

Finally eq.(C5) becomes

$$\varepsilon_{el}(Q) = 1 + \frac{\beta f(u)}{2u^2} - \frac{\beta}{4u}\int_{1-2u}^{1+2u} AV(x)\,x \ \ell n\ g\ dx \qquad \text{(C6)}$$

The case u > .5 is treated in a similar manner, and when combined with the case u < .5 gives eq.(2.45).

Appendix D. Expansions in Legendre Polynomials and Averages

We expand a function $S(\mu)$ of $\mu = \cos\Theta$ in Legendre polynomials

$$S(\mu) = \sum_{\ell=o}^{\infty} f_\ell P_\ell(\mu) \tag{D1}$$

where the coefficients are given by

$$f_\ell = \frac{2\ell+1}{2}\int_{-1}^{+1} P_\ell(\mu) S(\mu)\, d\mu$$

and $P_o(\mu) = 1$, $P_1(\mu) = \mu$, $P_2(\mu) = \frac{1}{2}(3\mu^2-1)$, . . .

$$\text{for } \ell = 0 \qquad f_o = \frac{1}{2}\int_{-1}^{+1} S(\mu)\, d\mu \tag{D2}$$

Now the average over a sphere is given by

$$\langle\ \rangle_{av} = \frac{1}{4\pi}\int d\Omega$$

$$= \frac{1}{4\pi}\int_o^{2\pi} d\phi \int_o^{\pi} \sin\Theta\, d\,\Theta$$

$$= \frac{1}{2}\int_{-1}^{+1} d\mu$$

where $\mu = \cos\ \Theta$. So if we have a function $S(\mu)$, the average value is given by

$$\left\langle S(\mu) \right\rangle_{av} = \frac{1}{2}\int_{-1}^{+1} S(\mu)\, d\mu \qquad \text{(D3)}$$

Comparing eq. (D3) with eq. (D2) we see that taking the average over a sphere gives the same result as expanding in Legendre polynomials and keeping the zeroth term.

Appendix E

$$C_{xy}(\vec{q}) = \frac{4\pi e^2}{v} \sum_{\tau} \frac{(q_x+\tau_x)(q_y+\tau_y)}{|\vec{q}+\vec{\tau}|^2} \exp(-|\vec{q}+\vec{\tau}|^2/4\eta^2)$$

$$+ e^2 \sum_{\ell \neq o} \exp(i\vec{q}\cdot\vec{\ell}) \left[\delta_{xy} \left\{ \frac{\phi(\eta\ell)}{\ell^3} + \frac{2}{\sqrt{\pi}\ell^2} \exp(-\eta^2\ell^2) \right\} \right.$$

$$\left. - \frac{\ell_x \ell_y}{\ell^2} \left\{ \frac{3\phi(\eta\ell)}{\ell^3} + \frac{6\eta}{\sqrt{\pi}\ell^2} \exp(-\eta^2\ell^2) + \frac{4\eta^3}{\sqrt{\pi}} \exp(-\eta^2\ell^2) \right\} \right]$$

$$- \frac{4e^2}{3\sqrt{\pi}} \eta^3 \delta_{xy} + \frac{4\pi e^2}{3v} \delta_{xy}$$

where $\phi(z) = 1 - \frac{2}{\pi} \int_o^z e^{-t^2} dt$

We have included the contribution $\frac{4\pi e^2}{3v} \delta_{xy}$ in C_{xy} rather than in E_{xy}, η is the parameter to be chosen to make both series converge quickly and $\vec{\ell}$ is a vector of the direct lattice.

Appendix F. The Difference between the "proton-proton" and the "proton-electron" Dielectric Functions

In an interacting electron gas the screened potential experienced by an external test charge (not an electron) is different from the screened potential experienced by an electron, since the electron experiences an extra field, the effective exchange and correlation field. To describe both situations one defines a "proton-proton" and a "proton-electron" dielectric function.

Ballentine (B67) considers a homogeneous interacting electron gas to which is applied an external sinusoidal potential $V_{ext}(\vec{Q})$ of wave vector $\vec{Q}$ (in the case of lattice vibrations V_{ext} is the perturbing ionic potential). An electrostatic potential $V_H(\vec{Q})$ is set up by the induced electron distribution (fig.(f1)).

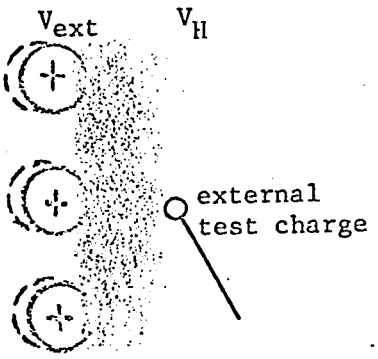


fig.(f1)

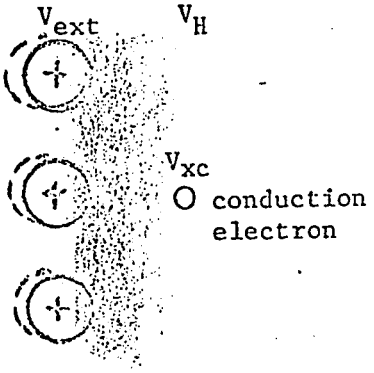


fig.(f2)

The resulting screened potential experienced by an external test charge (not an electron) is $\frac{V_{ext}}{\epsilon_{pr}}$ and is given by

$$V_{ext} + V_H = \frac{V_{ext}}{\varepsilon_{pr}} \qquad \text{(F1)}$$

where ε_{pr} is called the "proton-proton" dielectric constant.

Now the resulting potential experienced by a conduction electron (fig.(f2)) is $\frac{V_{ext}}{\varepsilon_{el}}$ and is given by

$$V_{ext} + V_H + V_{xc} = \frac{V_{ext}}{\varepsilon_{el}} \qquad \text{(F2)}$$

where ε_{el} is called the "proton-electron" dielectric constant and exchange and correlation effects are fully taken into account by V_{xc} which is a function of the total electron density. Combining eqs.(F1) and (F2) we get

$$\frac{V_{ext}}{\varepsilon_{pr}} + V_{xc} = \frac{V_{ext}}{\varepsilon_{el}} \qquad \text{(F3)}$$

Ballentine gives for V_{xc}

$$V_{xc} = -E \frac{V_{ext}}{\varepsilon_{el}} \qquad \text{(F4)}$$

where E is the exchange and correlation term (for example Geldart-Vosko's

$$E = -\frac{1}{2}\left[\frac{Q^2}{Q^2 + \xi k_F^2}\right] \chi).$$

Substituting (F4) into (F3) we obtain the relationship between the "proton-

proton" and the "proton-electron" dielectric constants.

$$\frac{1}{\varepsilon_{pr}} = \frac{1 + E}{\varepsilon_{el}} \qquad \text{(F5)}$$

We now write it in a form useful for equations encountered in lattice dynamics. Eq.(F5) yields

$$1 - \frac{1}{\varepsilon_{pr}} = \frac{\varepsilon_{el} - 1 - E}{\varepsilon_{el}} \qquad \text{(F6)}$$

and Ballentine gives $\varepsilon_{el} = 1 + \chi + E$ so that eq.(F6) becomes

$$1 - \frac{1}{\varepsilon_{pr}} = \frac{\chi}{\varepsilon_{el}} \qquad \text{(F7)}$$

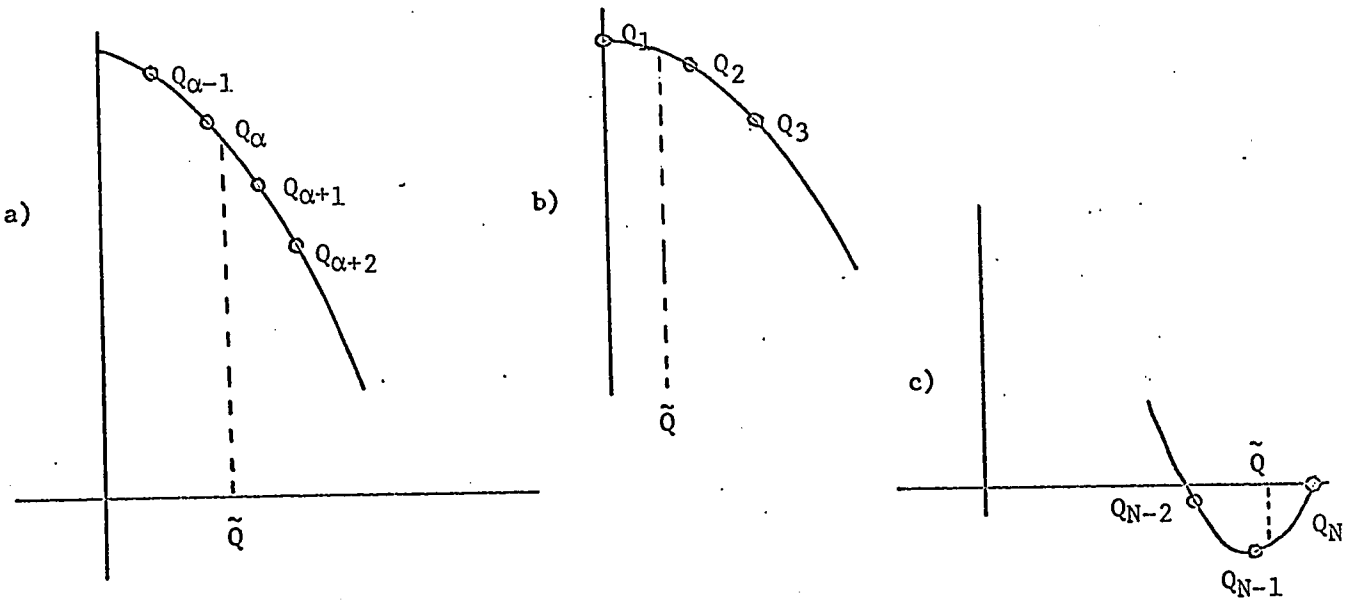
This is the relationship used for eqs.(4.15) and (4.16)

Appendix G. Details of the Non-Linear Least Squares Method

We start by discussing Lagrange interpolation for $f(Q)$. Take a value $\tilde{Q}$ for which $f(\tilde{Q})$ is to be evaluated

if $\tilde{Q} \geq Q_N$ then $f(\tilde{Q}) = 0$

if $\tilde{Q} < Q_N$ then three cases present themselves. Cases a), b) and c) as shown below



Case a) Let $Q_a = Q_{\alpha-1}$, $Q_b = Q_\alpha$, $Q_c = Q_{\alpha+1}$, $Q_d = Q_{\alpha+2}$

$$f(\tilde{Q}) = f(Q_a)\frac{(\tilde{Q}-Q_b)(\tilde{Q}-Q_c)(\tilde{Q}-Q_d)}{(Q_a-Q_b)(Q_a-Q_c)(Q_a-Q_d)} + \ldots + f(Q_d)\frac{(\tilde{Q}-Q_a)(\tilde{Q}-Q_b)(\tilde{Q}-Q_c)}{(Q_d-Q_a)(Q_d-Q_b)(Q_d-Q_c)}$$

Case b) Let $Q_a = Q_1$, $Q_b = Q_2$, $Q_c = Q_3$

$$\int(\tilde{Q}) = \int(Q_a) \frac{(\tilde{Q}-Q_b)(\tilde{Q}-Q_c)}{(Q_a-Q_b)(Q_a-Q_c)} + \int(Q_b) \frac{(\tilde{Q}-Q_a)(\tilde{Q}-Q_c)}{(Q_b-Q_a)(Q_b-Q_c)} + \int(Q_c) \frac{(\tilde{Q}-Q_a)(\tilde{Q}-Q_b)}{(Q_c-Q_a)(Q_c-Q_b)}$$

Case c) Let $Q_a = Q_{N-2}$, $Q_b = Q_{N-1}$, $Q_c = Q_N$

$\int(\tilde{Q})$ is given by the expression of case b)

We now discuss the non-linear least squares method (P65). The problem reduces to finding the minimum of the quantity

$$\Delta = \sum_i \left[\omega_{exp,i} - \omega(\vec{q}_i , C_1 , C_2 , \ldots, C_M)\right]^2 \qquad (G1)$$

with respect to the parameters C_1 , C_2 , ..., C_M. So we take the derivative with respect to C_k and set it equal to zero.

$$\frac{\delta\Delta}{\delta C_k} = 2\sum_i \left[\omega_{exp,i} - \omega(\vec{q}_i , C_1 , C_2 , \ldots, C_M)\right] \frac{\delta\omega}{\delta C_k} = 0$$

We expand $\omega(\vec{q}_i , C_1 , C_2 , \ldots, C_M)$ about the point $(\bar{C}_1 , \bar{C}_2 , \ldots, \bar{C}_M)$ where this set $\bar{C}_1 , \bar{C}_2 , \ldots, \bar{C}_M$ is a first approximation to the solution

$$\omega(\vec{q}_i,C_1,C_2,\ldots,C_M) = \omega(\vec{q}_i,\bar{C}_1,\bar{C}_2,\ldots,\bar{C}_M) + \frac{\delta\omega}{\delta C_1}\Delta C_1 + \ldots + \frac{\delta\omega}{\delta C_M}\Delta C_M \qquad (G2)$$

The next approximation to C_k is given by

$$C_k = \bar{C}_k + \Delta C_k$$

The problem is to determine the ΔC_k's such that successive approximations will lead us to the minimum for eq.(G1).

Substituting eq.(G2) into eq.(G1) we get

$$\sum_i \left[\omega_{exp,i} - \omega_i - \sum_\lambda \frac{\delta\omega}{\delta C_\lambda} \Delta C_\lambda \right] \frac{\delta\omega}{\delta C_k} = 0 \qquad \text{(G3)}$$

where $\omega_i = \omega(\vec{q}_i, \bar{C}_1, \bar{C}_2, \ldots, \bar{C}_M)$

Eq.(G3) can be written as

$$\sum_\lambda \left\{ \sum_i \frac{\delta\omega}{\delta C_\lambda} \frac{\delta\omega}{\delta C_k} \right\} \Delta C_\lambda = \sum_i \left[\omega_{exp,i} - \omega_i \right] \frac{\delta\omega}{\delta C_k} \qquad \text{(G4)}$$

Let $Z_{\lambda i} = \frac{\delta\omega}{\delta C_\lambda}$, eq.(G4) becomes

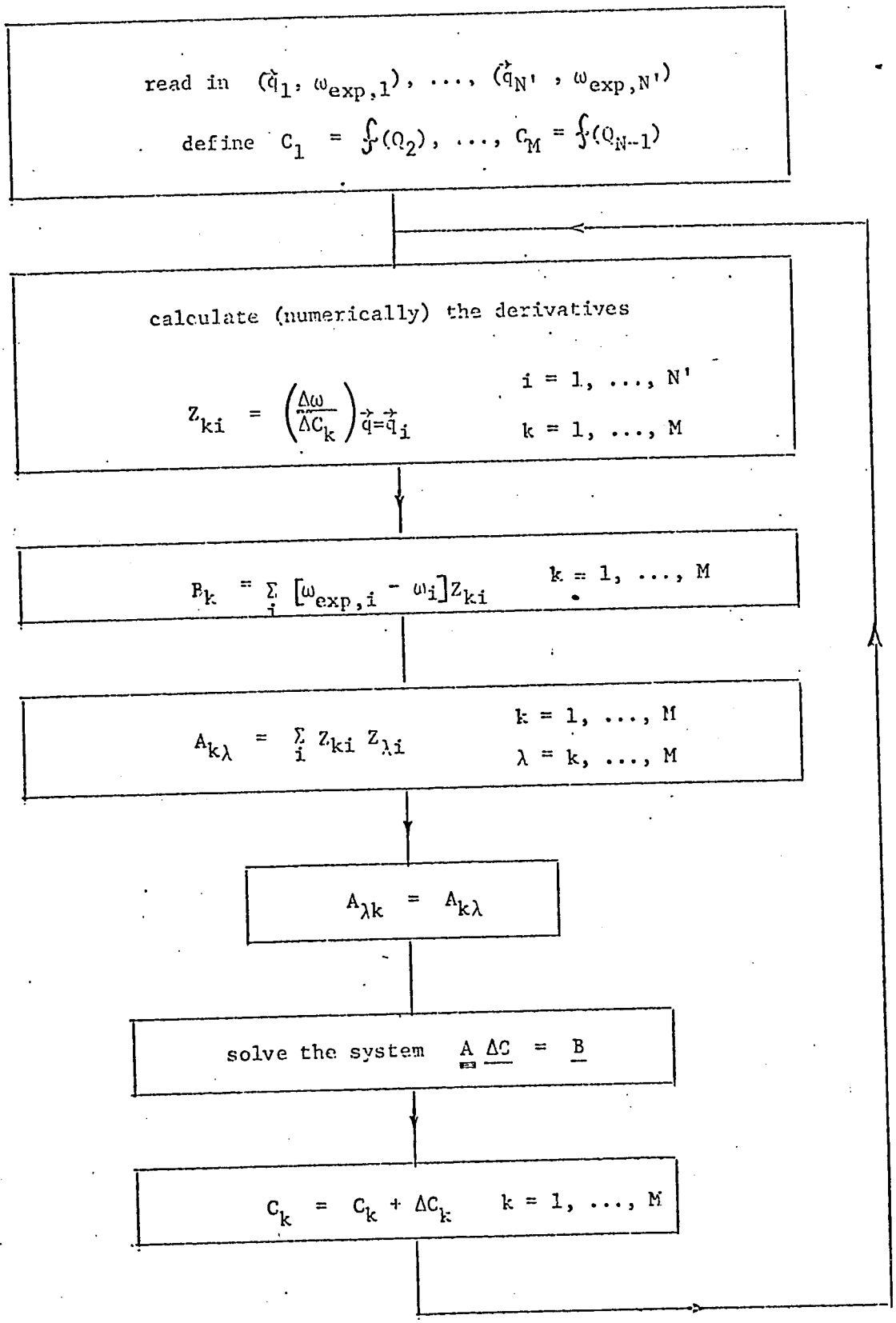
$$\sum_\lambda \left\{ \sum_i Z_{\lambda i} Z_{ki} \right\} \Delta C_\lambda = \sum_i \left[\omega_{exp,i} - \omega_i \right] Z_{ki} \qquad \text{(G5)}$$

Let $A_{\lambda k} = \sum_i Z_{\lambda i} Z_{ki}$ and $B_k = \sum_i \left[\omega_{exp,i} - \omega_i \right] Z_{ki}$,

eq.(G5) becomes

$$\sum_\lambda A_{\lambda k} \Delta C_\lambda = B_k \qquad \text{(G6)}$$

So the problem reduces to the solution of the linear system of eq. (G6) for the variables $\Delta C_1, \ldots, \Delta C_M$.


read in $(\vec{q}_1, \omega_{exp,1}), \ldots, (\vec{q}_{N'}, \omega_{exp,N'})$
define $C_1 = f(Q_2), \ldots, C_M = f(Q_{N-1})$
calculate (numerically) the derivatives
$Z_{ki} = \left(\frac{\Delta\omega}{\Delta C_k}\right)_{\vec{q}=\vec{q}_i}$ $i = 1, \ldots, N'$ $k = 1, \ldots, M$
$B_k = \sum_i [\omega_{exp,i} - \omega_i] Z_{ki}$ $k = 1, \ldots, M$
$A_{k\lambda} = \sum_i Z_{ki} Z_{\lambda i}$ $k = 1, \ldots, M$ $\lambda = k, \ldots, M$
$A_{\lambda k} = A_{k\lambda}$
solve the system $\underline{A}\,\underline{\Delta C} = \underline{B}$
$C_k = C_k + \Delta C_k$ $k = 1, \ldots, M$

REFERENCES

A59 E.Antončák, J.Phys.Chem.Solids, 10, 314 (1959)

A66 A.O.E.Animalu, F.Bonsignori and V.Bortolani, Nuovo Cimento, 44, 159 (1966)

A68 N.W.Ashcroft, J.Phys.C., 1, 232 (1968)

B37 J.Bardeen, Phys.Rev., 52, 688 (1937)

B53 D.Bohm and D.Pines, Phys.Rev., 92, 609 (1953)

B54 M.Born and K.Huang, Dynamical Theory of Crystal Lattices (Oxford University Press 1954)

B55 J.Bardeen and D.Pines, Phys.Rev., 99, 1140 (1955)

B55a A.B.Bhatia, Phys.Rev., 97, 363 (1955)

B55b A.B.Bhatia and G.K.Horton, Phys.Rev., 98, 1715 (1955)

B60 M.Bailyn, Phys.Rev., 117, 974 (1960)

B67 L.E.Ballentine, Phys.Rev., 158, 670 (1967)

B67a R.Blanchard and Y.P.Varshni, Phys.Letters 25A, 581 (1967)

C62 M.H.Cohen, J.Phys.Radium, 23, 643 (1962)

C63 W.Cochran, Proc.Roy.Soc., A, 276, 308 (1963)

C63a W.Cochran, Repts.Prog.Phys., 26, 1 (1963)

C65 W.Cochran, Inelastic Scattering of Neutrons (Bombay), Vol.1, p3 (1965)

C65a W.Cochran, in "Lattice Dynamics" (R.F.Wallis, ed.) p.83 (Pergamon Press, New York, 1965)

C66 R.A.Cowley, A.D.B.Woods, and G.Dolling, Phys.Rev., 150, 487 (1966)

C68 J.R.D.Copley, B.N.Brockhouse and S.H.Chen, Proc.IAEA Sym.Neutron Inelastic Scattering, Copenhagen, May 1968, Vol.I, 209

C68a L.Cheveau, Phys.Rev., 169, 496 (1968)

D53 J.de Launay, J.Chem.Phys., 21, 1975 (1953)

D54 J.de Launay, J.Chem.Phys., 22, 1976 (1954)

D56 J.de Launay, Solid State Physics, 2, 219 (1956)

D64 J.K.Darby, Thesis, The Electron-Phonon Interaction and Transport Properties of Sodium. University of Sheffield. Sept.1964

D64a B.Dayal and P.L.Srivastava, Proc.Roy.Soc., A277, 183 (1964)

D65 B.Dayal and P.L.Srivastava, Proc.Roy,Soc., A283, 394 (1965)

G63 D.E.Gray, American Institute of Physics Handbook (McGraw Hill, 1963)

G65 D.J.W.Geldart and S.H.Vosko, J.Phys.Soc. Japan, 20, 20 (1965)

G69 D.J.W.Geldart and R.Taylor, preprint (1969)

H35 H.Hellmann, Acta Physicochimica URSS, 1, 913 (1935)

H36 H.Hellmann and W.Kassatotschkin, Acta Physicochimica URSS, 5, 23 (1936)

H57 J.Hubbard, Proc.Roy.Soc. A243, 336 (1957)

H60 D.Hone, Phys.Rev. 120, 1600 (1960)

H64 V.Heine and I.Abarenkov, Phil.Mag., 9, 451 (1964)

H66 W.A.Harrison, Pseudopotentials in the Theory of Metals (W.A.Benjamin, Inc., New York, 1966)

H67 P.S.Ho and A.L.Ruoff, Phys.Stat.Sol. 23, 489 (1967)

H68 P.S.Ho, Phys.Rev., 169, 523 (1968)

J68 S.K.Joshi and A.K.Rajagopal, Solid State Physics, 22, 160 (1968)

K40 E.W.Kellermann, Phil.Trans.Roy.Soc., 238, 513 (1940)

K64 K.Krebs, Phys.Letters, 10, 12 (1964)

K65 K.Krebs, Phys.Rev., 138, A143 (1965)

K66 C.Kittel, Introduction to Solid State Physics, 3rd Edition (John Wiley,1966)

K67 L.Kleinman, Phys.Rev. 160, 585 (1967)

L63 J.Laval, in "Crystallography and Crystal Perfection" (Academic Press,1963)

L65 M.Lax, in "Lattice Dynamics" (R.F.Wallis, ed.) p.179 (Pergamon Press, 1965)

M63 A.A.Maradudin, E.W.Montroll, and G.H.Weiss, Theory of Lattice Dynamics in the Harmonic Approximation. (Academic Press, New York 1963)

N65 M.A.E.Nutkins, Proc.Phys.Soc., 86, 181 (1965)

P58 W.B.Pearson, "Handbook of Lattice Spacings and Structures of Metals" (Pergamon Press, 1958)

P59 J.C.Phillips and L.Kleinman, Phys.Rev., 116, 287 (1959)

P63 David Pines, Elementary Exitations in Solids, p.108 (W.A.Benjamin Inc.1963)

P65 Ralph H.Pennington, Introductory Computer Methods and Numerical Analysis (Macmillan Co., New York 1965)

R61 S.Raimes, The Wave Mechanics of Electrons in Metals, p.293 (North-Holland 1961)

S40 F.Seitz, The Modern Theory of Solids (McGraw Hill 1940)

S51 J.C.Slater, Phys.Rev., 81, 385 (1951)

S61 R.A.Smith, Semiconductors (Cambridge University Press 1961)

S63 L.J.Sham and J.M.Ziman, Solid State Physics, 15, 221 (1963)

S63a P.L.Srivastava and R.S.Srivastava, Proc.Phys.Soc., 81, 586 (1963)

S63b P.K.Sharma and S.K.Joshi, J.Chem.Phys., 39, 2633 (1963)

S64 P.K.Sharma and S.K.Joshi, J.Chem.Phys., 40, 662 (1964)

S64a R.S.Srivastava and B.Dayal, Prog.Theor.Phys., 31, 167 (1964)

S65 Alf Sjölander, Symposium on Inelastic Scattering of Neutrons by Condensed Systems, p.29 (Brookhaven National Laboratory 1965)

S65a P.L.Srivastava and B.Dayal, Phys.Rev., 140, A1014 (1965)

S65b L.J.Sham, Proc.Roy.Soc., A283, 33 (1965)

S66 T.Schneider and E.Stoll, Phys.Kondens.Materie, 5, 331 (1966)

S66a T.Schneider and E.Stoll, Phys.Kondens.Materie, 5, 364 (1966)

S67 W.M.Shyu and G.D.Gaspari, Phys.Rev., 163, 667 (1967)

S68 W.M.Shyu and G.D.Gaspari, Phys.Rev., 170, 687 (1968)

T58 T.Toya, J.Res.Inst.Catalysis, Hokkaido Univ., 6, 183 (1958)

T58a T.Toya, J.Res.Inst.Catalysis, Hokkaido Univ., 6, 161 (1958)

T59 T.Toya, J.Res.Inst.Catalysis, Hokkaido Univ., 7, 60 (1959)

T61 T.Toya, J.Res.Inst.Catalysis, Hokkaido Univ., 9, 178 (1961)

T68 H.Takahashi, Phys.Rev. 172, 747 (1968)

V64 S.H.Vosko, Phys.Letters, 13, 97 (1964)

V65 S.H.Vosko, R.Taylor and C.H.Keech, Can.J.Phys., 43, 1187 (1965)

W33 E.P.Wigner and F.Seitz, Phys.Rev., 43, 804 (1933)

W62 A.D.B.Woods, B.N.Brockhouse, R.H.March, A.T.Stewart, and R.Bowers, Phys.Rev., 128, 1112 (1962)

Z62 J.M.Ziman, Electrons in Metals, Taylor and Francis Ltd.

Z64 J.M.Ziman, Principles of the Theory of Solids (Cambridge University Press 1964)

Z64a J.M.Ziman, Adv.Phys., 13, 89 (1964)

POST ORAL DISCUSSION

This section was written after the oral examination to discuss a number of points made by the examiners during the oral. The examining board consisted of Dr. R. A. Cowley of Chalk River Nuclear Laboratories, Dr. C. B. Benson, Dr. R. C. Smith and Dr. R. G. Tross.

1 (a). Discussion of Bailyn's basic equation.

The Hartree-Fock wavefunction used in deriving Bailyn's basic equation contains the implicit assumption that the electrons are independent particles, spin-spin correlation being taken into account only. Later on dynamical correlation is introduced by screening the electron-electron interaction by means of a suitable dielectric function. Furthermore, the Bailyn equation is an approximation to a more complicated equation derived in Sham and Ziman (S63). In their notation

$\vec{K}$ denotes the scattering vector,

the dielectric function is defined as the sum of the series;

$$\epsilon^{-1}(\vec{k},\vec{k}+\vec{K}) = 1 + \sum_{K} A_{k,K}(\vec{K}) + \sum_{KK'} A_{k,K}(\vec{K}) A_{K,K'}(\vec{K}) + \cdots$$

where

$$A_{k,k}(\vec{K}) = \frac{n(\vec{k}) - n(\vec{k}+\vec{K})}{\mathcal{E}(\vec{k}) - \mathcal{E}(\vec{k}+\vec{K})} \left\{ \frac{4\pi e^2}{N K^2} - V_s(\vec{k}+\vec{K},\vec{k},\vec{k},\vec{k}+\vec{K}) \right\}$$

and

$$V_s(\vec{k}+\vec{K},\vec{k},\vec{k},\vec{k}+\vec{K}) = \frac{4\pi e^2}{N\{(\vec{k}-\vec{k})^2 + k_s^2\}}$$

Bailyn (and Hone) approximate ϵ^{-1} to

$$\epsilon^{-1}(\vec{k},\vec{k}+\vec{K}) = 1 + \sum_{K} A_{k,K}(\vec{K})$$

1 (b) The extent to which the Ward-Pitayevski identities are satisfied, comparison with the results of Gell-Mann and Brueckner.

We start by introducing certain definitions and relations. Following Geldart and Taylor (G69) we write the dielectric function in the form

$$\epsilon = 1 + \frac{4\pi e^2}{Q^2}\Pi \qquad (1)$$

Following Geldart and Vosko (G66) we introduce the definition

$$\Pi^{\infty} = \lim_{\omega \to 0} \lim_{Q \to 0} \Pi \qquad (2)$$

The limits being taken in the order shown above. Π^{∞} is known as the screening-constant. There exists an exact relationship between the compressibility of the electron gas κ and the screening constant Π^{∞} (N63);

$$\frac{\kappa}{\kappa_0} = \frac{\Pi^{\infty}}{\Pi_0^{\infty}} \equiv \frac{1}{G} \qquad [3]$$

κ and Π^{∞} represent the compressibility and the screening constant for the interacting electron gas.

κ_0 and Π_0^{∞} the corresponding quantities for the non-interacting electron gas.

Now $$\lim_{\omega \to 0} \Pi_0 = \frac{mk_F}{\pi^2\hbar^2} f(u) \qquad (4)$$

where $$f(u) = \frac{1}{2} + \frac{1-u^2}{4u} \ln\left|\frac{1+u}{1-u}\right| , \qquad u = Q/2k_F$$

thus $$\Pi_0^{\infty} = \frac{mk_F}{\pi^2\hbar^2} \qquad (5)$$

Now let us study Hubbard's dielectric function and determine L_H as defined by eq. (3).

$$\epsilon_H = 1 + \frac{4\pi e^2}{Q^2} \Pi_H \tag{6}$$

where

$$\Pi_H = \frac{\Pi_0}{1 - \frac{1}{2} \frac{4\pi e^2}{Q^2 + \xi_H k_F^2} \Pi_0} \tag{7}$$

and

$$\xi_H = 1 + \frac{4\pi e^2}{k_F^2} \Pi_0^\infty \tag{8}$$

which we rewrite

$$\xi_H = 1 + 4\lambda \tag{9}$$

where

$$\lambda = \frac{\alpha r_s}{\pi} \qquad \alpha = (4/9\pi)^{1/2} = .521$$

Now using eqs. (3), (5) and (7) we obtain

$$L_H \equiv \frac{\Pi_0^\infty}{\Pi_H^\infty} = \frac{1+2\lambda}{1+4\lambda} \tag{10}$$

We now list various expressions for L as obtained by different methods and various authors.

Hartree-Fock (P66) $$L_{HF} = 1 - \lambda \tag{11}$$

Random Phaze Approximation (P66)

$$L_{RPA} = 1 - \lambda - \lambda^2(1-\ln 2)\ln\frac{\pi\lambda}{\alpha} \tag{12}$$

Gell-Mann and Brueckner (G67)

$$L_{GB} = 1 - \lambda - (1-\ln 2)\lambda^2 \tag{13}$$

Glick (G63)

$$L_G = 1 - \lambda\left[1 - \lambda \ln\left(\frac{1+\lambda}{\lambda}\right)\right] \tag{14}$$

Osaka (O62)

$$L_{Os} = 1 - \frac{\lambda}{(1-\lambda/3)}\left\{1 - \frac{\lambda}{(1-\lambda/3)}\ln\left[\frac{(1-\lambda/3)+\lambda}{\lambda}\right]\right\} \tag{15}$$

These estimates of L are plotted as a function $\frac{\phi_\lambda}{\lambda^\pi}$ in Fig. (J1), which is

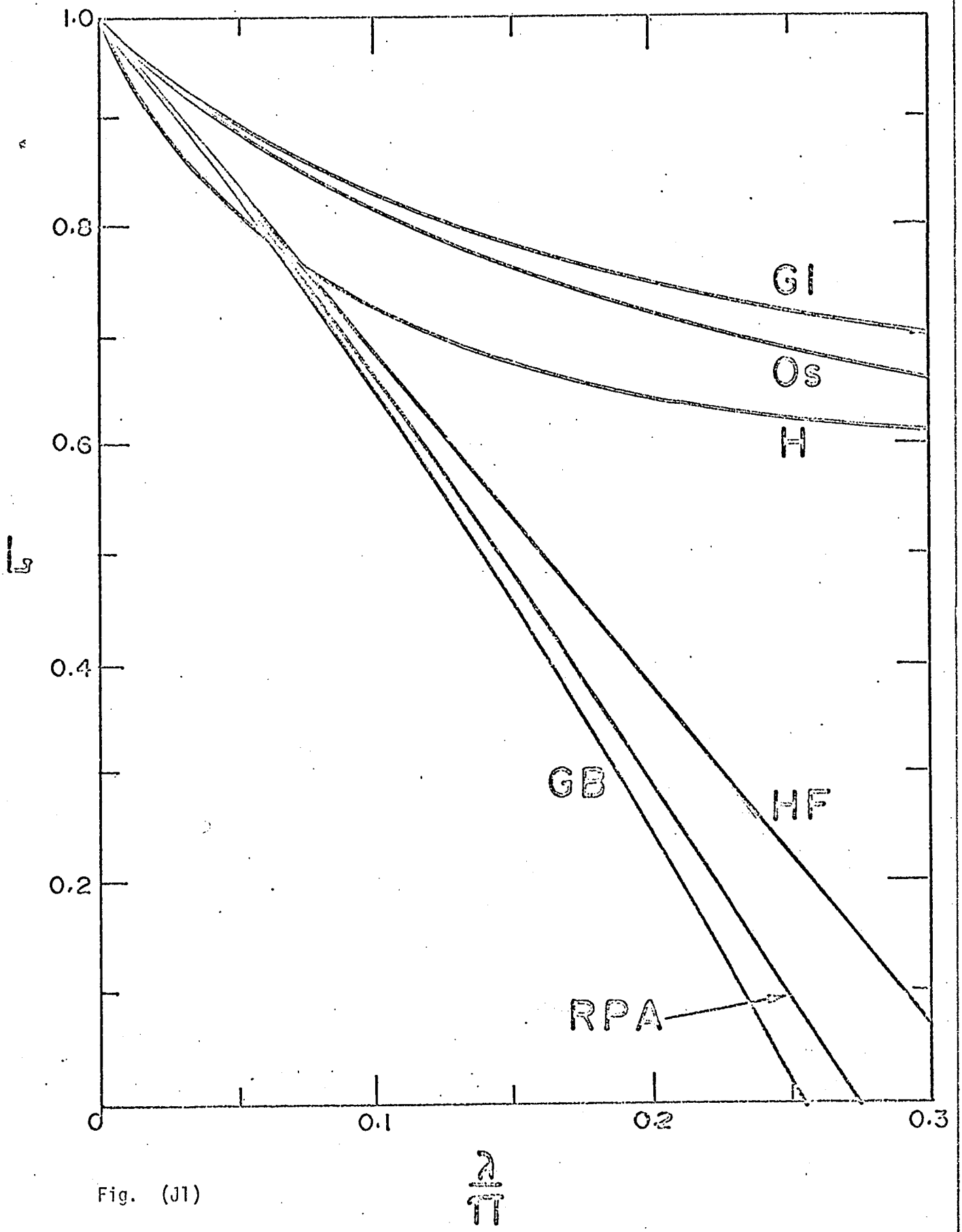


Fig. (J1)

reproduced from ref. (G66). We now discuss the modification of the ξ parameter in eq. (7) to force the $Q \to 0$ limit of Π_H to agree with the static limit implied by the relation between the compressibility and the screening constant as given by eq. (3). Hubbard's expression may be written as

$$\epsilon_H = 1 + \frac{\chi}{1 - \frac{1}{2}\frac{Q^2}{Q^2 + \xi k_F^2}\chi} \qquad (16)$$

where

$$\chi = \frac{4\pi e^2}{Q^2}\Pi_0$$

Now as $Q \to 0$, $\chi \to k_s^2/Q^2$ so that eq. (16) can be written

$$\epsilon_H \to 1 + \frac{\chi}{1 - \frac{1}{2}\frac{k_s^2}{\xi k_F^2}} \qquad (17)$$

since $\frac{k_s^2}{k_F^2} = 4\lambda$, eq. (17) becomes

$$\epsilon_H \to 1 + \frac{\chi}{1 - \frac{2\lambda}{\xi}} \qquad (18)$$

Now the dielectric function ϵ_0 for the non-interacting electron gas is

$$\epsilon_0 = 1 + \chi \qquad (19)$$

So that taking the limit $Q \to 0$ one obtains

$$\frac{\Pi_0^\infty}{\Pi_H^\infty} \equiv \lfloor = 1 - \frac{2\lambda}{\xi} \qquad (20)$$

thus yielding

$$\xi = \frac{2\lambda}{1 - L} \tag{21}$$

If we choose $L = L_H = \frac{1+2\lambda}{1+4\lambda}$

we obtain

$$\xi = \xi_H = 1 + 4\lambda$$

as given by eq. (9). So that we can take any estimate of L and fix ξ such that any curve of Fig. (J1) can be reproduced. For example if we choose $L = L_{GB}$ then the expression for Π_H given by eq. (7) reproduces the results of Gell-Mann and Brueckner.

We now discuss what must be done to our dielectric function

$$\epsilon_{Ours} = 1 + \frac{\chi}{1 - \frac{1}{2}\frac{\chi}{1+\chi}} \tag{22}$$

to satisfy the fundamental relations between the compressibility and the screening constant. To accomplish this, we must treat $\beta = \frac{1}{2}\frac{k_s^2}{k_F^2}$ as a parameter (in a similar manner as Geldart and Vosko's method of fixing ξ) instead of employing its standard value $\beta = \frac{1}{2}\frac{k_{TF}^2}{k_F^2}$ where k_{TF} is the inverse Thomas-Fermi length.

Let us use β' to denote the variable parameter which will be adjusted, i.e. $\beta' = \frac{1}{2} \frac{k_s^2}{k_F^2}$ and reserve the symbol β for the fixed value determined by the Thomas-Fermi screening length, namely $\beta = \frac{1}{2} \frac{k_{TF}^2}{k_F^2}$. We thus write eq. (22) as

$$\epsilon_{Ours} = 1 + \frac{\chi'}{1 - \frac{1}{2}\frac{\chi'}{1+\chi'}} \tag{23}$$

where

$$\chi' = \frac{\beta' f(u)}{2u^2} \qquad \text{and} \quad u = Q/2k_F$$

As $Q \to 0$

$$\epsilon_{Ours} \to 1 + 2\chi' \tag{24}$$

Now

$$\epsilon_0 \to 1 + \chi \tag{25}$$

where

$$\chi = \frac{\beta f(u)}{2u^2}$$

so that

$$\frac{\Pi_0^\infty}{\Pi_{Ours}^\infty} \equiv L_T = \frac{\beta}{2\beta'} \tag{26}$$

thus

$$\beta' = \frac{\beta}{2L_T} \tag{27}$$

Choosing $L_T = L_{GB}$, eq. (23) for ε_{ours} will automatically reproduce the results of Gell-Mann and Brueckner.

Eq. (27) can be obtained in a different way. One of the Ward identities is (L69)

$$\epsilon \to 1 + (K/K_0)\, k_{TF}^2 / Q^2 \tag{28}$$

which can be written as

$$\epsilon \to 1 + (1/L_T)\, \beta/2u^2 \tag{29}$$

Our dielectric function gives

$$\epsilon_{ours} \to 1 + 2\chi' \tag{30}$$

which can be written

$$\epsilon_{ours} \to 1 + \beta'/2u^2 \tag{31}$$

Identifying eq. (29) with eq. (31) we get

$$\beta' = (1/L_T)\, \beta/2$$

thus obtaining

$$\beta' = \frac{\beta}{2L_T}$$

2. Why eℓ-pr screening was used instead of eℓ-eℓ screening.

We were not aware that eℓ-pr screening was different from eℓ-eℓ screening. I realized the difference during the defence (when the question was raised). Heine and Abarenkov point out (H64) that when exchange and correlation effects are included, one must distinguish between three different dielectric functions

i) pr-pr

ii) pr-eℓ

iii) eℓ-eℓ

This makes little difference in the results since

$$\epsilon_{el} \approx 1 + \chi(q)$$

is a good approximation to describe eℓ-eℓ screening. (It is better than the long wavelength approximation $\epsilon_{e\ell} \simeq 1 + k_s^2/Q^2$).

3. The derived potential V(Q) should have $\frac{\partial V(Q)}{\partial Q} = 0$ for $Q = 0$.

Two possible ways of having $\frac{\partial V(Q)}{\partial Q} = 0$ for $Q = 0$ are

i) Choosing an analytic form which has zero derivative at $Q = 0$.

ii) Defining V(Q) at a few negative values of Q in a way symmetric with the positive values, thus making V(Q) an even function which must have zero derivative at $Q = 0$.

REFERENCES

G57 M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957).

G63a A. J. Glick, Phys. Rev. 129, 1399 (1963).

G66 D. J. Geldart and S. H. Vosko, Can. J. Phys. 44, 2137 (1966).

G69 D. J. W. Geldart and R. Taylor, preprint (1969).

H64 V. Heine and I. Abarenkov, Phil. Mag. 9, 451 (1964).

L69 D. C. Langreth, Phys. Rev. 181, 753 (1969).

N63 P. Nozières, Theory of Interacting Fermi Systems (W. A. Benjamin, Inc., New York, 1963).

O62 Y. Osaka, J. Phys. Soc. Japan 17, 547 (1962).

P66 D. Pines and P. Nozières, The Theory of Quantum Liquids, Vol. I (W. A. Benjamin, Inc., 1966).

S63 L. J. Sham and J. M. Ziman, Solid State Physics 15, 221 (1963).

Curriculum Vitae

Name: Robert Blanchard

Address: Department of Physics,
University of Ottawa,
Ottawa 2, Ont.

Date and place of birth: 20 May 1941, Ottawa

Married

Education:

until 1959 - high school
1959-at present - University of Ottawa as follows:

1959-60 Pre Science
1960-64 B.Sc.(Hon.) Physics
1964-65 Graduate work - in the Mathematics dept.
1965-66 M.Sc. - Physics
1966-at present: Ph.D. - Physics

Degrees:

1964 B.Sc.(Hon.) (Physics) Dean's Honour List
1966 M.Sc.(Physics) Magna cum Laude

M.Sc.thesis: "The Lattice Dynamics of Diamond on the Basis of Cochran's Model."