THE MOTION OF AN ION IN AN ELECTRON GAS

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ABSTRACT

We give a semi-classical treatment of the problem of electrical conduction around a charged impurity ion in a metal. As the electrons flow past the ion they are scattered by its screened Coulomb potential and so introduce a velocity dependent distribution of charge. This charge distribution leads, through the Poisson equation, to a modification of the potential surrounding the ion through which the electrons are initially scattered; we look for a self-consistent or simultaneous solution to the Boltzmann and Poisson equations. This final velocity dependent charge distribution induces an electric field at the ion, so exerting a force on that ion. We identify two effects: (i) a screening force acting so as to reduce the effect of the external field on the ion, (ii) a drift force resulting from the direct collisions between electron and ion.

The process is described by a Boltzmann Transport equation which we solve at large distances from the ion. We derive the Green's Function for the equivalent integral equation, and then solve that equation by means of a Fourier Transform. In this technique we do not assume as in previous approaches that the ion is stationary or that its charge is small. The evaluation of the Green's Function does however involve the construction of an orbit model in which all scattered electrons pass through the ion itself and we do not expect this model to be of any use inside the screening radius.

We turn to a method of expansion by spherical harmonics, suggested by Das in his thesis, in the hope that it may be of use at short range. In understanding a paradox

of the method we lose a criterion for convergence and our confidence in the method. To do this we consider the electron mean free path to be infinite in this short range region. In this limit a quantum mechanical calculation of the self-consistent field gives a result identical to that from a classical weak charge calculation due to Peierls, in the same limit, with the significant addition of a cut-off in momentum space at twice the Fermi-momentum. It is this cut-off, for which Peierls had argued on physical grounds, that eliminates a divergence at the origin. We use it to calculate the force.

We find that we may add Peierls' result where the Green's Function method is too insensitive. There are then three extra terms in the force, two due to drift and one to screening. However, the term we interpret as a screening correction may for large enough charge on the ion become greater than the direct field force. This may be due to an error in our interpretation as screening, or in the calculation itself. If it is the latter we propose a further calculation to check. In as far as the force on the ion derived in this thesis may be larger than the direct field force there is no disagreement with experimental data. Until we can understand the screening problem the result is not suitable for a detailed comparison with experiment.

CHAPTER I

I.i The Nature of the Force

When an impurity is embedded in a metal it may be ionised. It then behaves as a charged particle whose mass is several thousand times the electron mass. The ion is bound to the lattice by strong electrostatic forces. The static problem of an ion in an electron gas was treated classically by Debye and Hückel. They deduced that the electrons redistribute themselves to form a screening cloud around the ion. These electrons are not bound to the ion but linger in the neighbourhood to maintain electrical neutrality in the metal.

We are concerned with what happens to the electron distribution when we apply an external electric field. Experimentally many light impurities in host metals are found to migrate through the lattice. So there is evidence of a force on these impurities which is large enough to drag them away from their lattice sites. In this introduction

we shall be discussing the evidence for such a force and the previous attempts to derive expressions to explain it. Finally, we discuss the model we shall employ in this thesis.

We can immediately understand the mechanisms with which we shall explain the force. The ion with its screening charge is contrasted with a free atom in a vacuum or in a dielectric medium. There are then no free electrons and the atom maintains neutrality by binding the electrons to its core. If we apply an electric field to the dielectric the atom is polarized. The bound electrons distribute themselves so that they induce a field at the core which just cancels the external field. In the metal the screening charge need not necessarily become polarized to the same extent for it is not bound to the ion. In this case there is also a force which arises from the collisions between the charge carriers and the ion. It is these two forces that we shall estimate here.

The difference between the force resulting from a polarization of the screening charge and that from the drift may be understood if we consider the sign of the charge carriers and the ion to be the same. In this case the screening and drift forces would be in opposition. The signs of the dipole charge distributions arising in each case are shown in Fig I. The difference will appear mathematically in the order of the charge Z on the ion, and the charge e_c of the carrier. The screening force will be odd in Z and even in e_c and the drift force will be even in Z and odd in e_c. We shall find both types of force, and we do this by looking for an expression for the electric field at the ion due to the redistribution of the carriers.

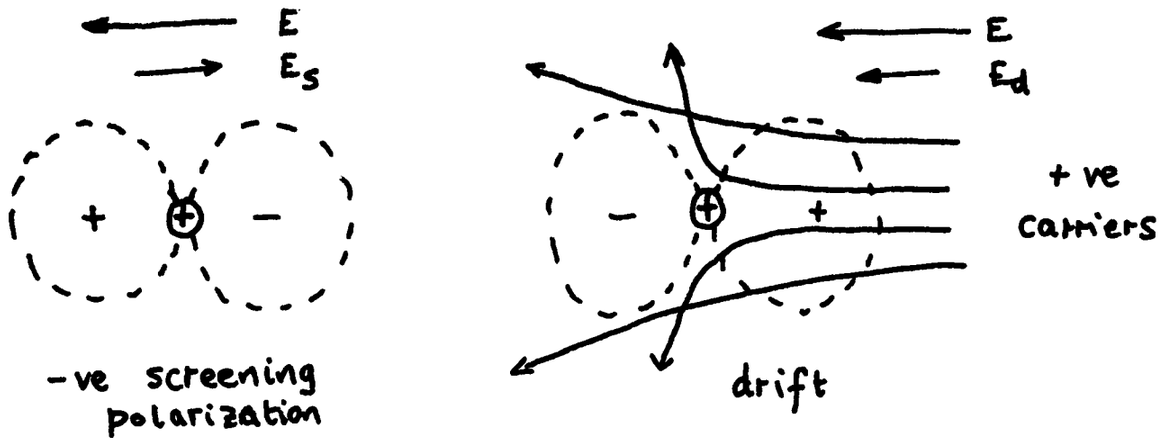


Fig I.i

I.ii Experimental evidence

Coehn and Specht (1930) showed that a few atomic percent of hydrogen dissolved in the transition metal palladium migrated to the cathode. In this case the protons followed the direct field force. In spite of the evidence of A.J. Maeland (1968) through neutron diffraction studies that these ions do take up lattice sites the total force was greater than that binding them to the lattice.

Kalinovich (1961) investigated the diffusion of carbon ions in γ-iron. He was able to substitute radioactive C^{14} in a section of wire and observe the movement of this radioactive region along the wire when a current was flowing. By measuring the diffusion constant he related this process to an "effective charge" on the carbon ions Z^*e. He found $Z^* \sim 10$ at a temperature of 1000°C. He also noticed a decrease in Z^* for increasing temperature which he attributed to the decrease in mean free path l in an expression for Z^* derived by Fiks (1959):

$$Z^* = Z - n_e \sigma_e l_e + n_h \sigma_h l_h \qquad \text{(I.ii.1)}$$

n_e is the electron density, and σ_e is the cross-section for scattering from the ion. The subscript h applies to holes . For carbon in γ-iron Kalinovich finds an effective charge of 49.3. He also discusses migration to the cathode for carbon in nickel and quotes results in which oxygen ions in β-titanium and nitrogen ions in γ-iron both migrate to the anode during electrical transport.

In his analysis Fiks draws an analogy with a defect in a nearly perfect crystal. This has been persued by Routbort (1968) in measuring the "electromigration" in Zinc single crystals. He measures an effective charge from the diffusion coefficient which does not give agreement with Fiks' result. The Fiks' formula (I.i.i) lends itself to easy interpretation when considered with the Hall coefficient. In metals with a positive Hall coefficient the hole drift impinging on a positive ion would result in mass transport to the cathode. In the case of a negative Hall coefficient the direction of mass transport will depend on the relative magnitudes of the drift force and the direct field force. This is in agreement with α-iron and cobalt where there is a large positive Hall coefficient, and in these metals there is mass flow to the cathode. This may explain some of Kalinovich's results, but Routbort's own case is not explained. He finds no simple relation between the signs of the effective charges and the Hall coefficients along two of the crystal axes. Furthermore Kuz'menko (1962) used the radioactive tracer technique to show that

	Z^*	t°C
Zn	4·3	370
Cd	5·1	250
Pb	46·6	250

and in spite of a small positive Hall coefficient there was mass flow to the anode. Routbort concludes that the electromigration may be too sensitive to the band structure which is responsible for the competition between the contributions from electrons and holes.

Before going on to consider the force in detail we shall mention a curious result which may be related to the process under discussion. Huntington and Ho (1963) studied gold and copper wires under a microscope and observed the movement of a scratch on the surface as a current flowed. They found their results independent of the size of the scratch and related them to the force on the surrounding atoms from the "electron wind". At various temperatures they find that for gold the " wind" always dominates the movement. But for copper the direction of travel of the marker changes sign above 1000^{o}C to give mass flow to the cathode. They comment: "The cause of this puzzling behaviour is still a matter of conjecture. There appears, however, to be little doubt of the reality of the effect since our results corroborate the findings of Wever (1956) on copper".

In conclusion we should say that in all these experiments the conduction process is complex. Palladium, iron, nickel, etc. are transition metals with conduction by both holes and electrons dominated by the s-d transition. The "moving scratch" is a long way from an isolated dislocation. The ideal experiment for this analysis would be an investigation into hydrogen ion mobility in a metal like sodium which is close to the free electron model employed.

I.iii Models from the literature

The force has been discussed in terms of scattering from a free ion by V.B. Fiks (1959). The marker motion on the wire was analysed as a similar problem by Huntington and Grone (1961) using the Bloch waves of the electrons. A self-consistent field was derived by Friedel and Bosvieux (1962) using perturbation theory. All these analyses have their drawbacks. Both Fiks and Huntington and Grone are unable to include the effect of the correction to the potential arising from the redistribution of the electrons after scattering. In the methods involving perturbation theory the problem reduces to evaluation of the static dielectric susceptibility, but necessitates linearization of the screening potential with respect to the charge. Fiks is the only case which recognises the motion of the impurity and even there is unable to make any useful conclusions.

The interaction force was first discussed by Fiks (1959). He considers a free electron model in which the electron distribution in the presence of a field E, or drift velocity u, is given by:

$$f = f_0 - eE \frac{l}{v} v_z \frac{\partial f_0}{\partial E} = f_0 - u p_z \frac{\partial f_0}{\partial E} \qquad \text{(I. iii. 1)}$$

f_0 is here the Fermi-Dirac distribution for electrons in the metal. Fiks obtains an expression for the force by integrating the momentum transfer $(p_z - p_z')$ over this distribution. He gives his result in terms of the cross-section σ for scattering off the stationary ion, the electron density n, and the electron mean free path l:

$$F = eE(z - n\sigma l)$$

Fiks goes on to suggest that with substantial distortion of the lattice and the electronic structure of the ion the

moving impurity will cause more scattering than an isolated ion. It is then necessary to calculate the cross-section σ^* for scattering from the ion when it is at a saddle point in the lattice. The difficulties involved in this calculation render this analysis of limited value. He did introduce the "effective charge" z^* on the ion:

$$z^* = z - n\sigma l$$

which as observed in section I.i may be extended to two-band conductors.

Huntington and Grone (1961) compared the problem of the movement of a scratch on the surface of a wire to our problem of the impurity or vacancy inside the wire. They wrote the momentum transfer in terms of the group velocity of the Bloch waves before and after scattering.

$$\delta M_x = \frac{m_o}{\hbar}\left(\frac{\partial E}{\partial k_x'} - \frac{\partial E}{\partial k_x}\right)$$

The transition probability across the defect was written in terms of the parameter τ_d :

$$\frac{dM_x}{dt} = \frac{m_o}{\tau_d \hbar}\int \frac{\partial E}{\partial k_x} f(k)\, \frac{d^3\underline{k}}{4\pi^3}$$

Since the current is given by:

$$j_x = -\frac{e}{4\pi^3\hbar}\int f(k)\, \frac{\partial E}{\partial k_x}\, d^3\underline{k}$$

the force may be expressed in terms of the resistivity ρ_d due to the defects, and effective mass m^* :

$$F_x = -e E_x z \frac{N\rho_d}{\rho N_d}\frac{m_o}{|m^*|}$$

In a later paper (1963) Huntington and Ho replaced m_e by m^*. This result is then similar to that obtained by Friedel and Bosvieux which we are about to discuss. The main disadvantage in this analysis is that it does not take account of the redistribution of electrons around the imperfection, particularly when it is moving. The agreement with Friedel and Bosvieux is discussed after the discussion of their analysis.

The quantum mechanical calculation of Friedel and Bosvieux (1962) is the most detailed analysis to date. Their method is to consider the impurity potential as a perturbation on the ground state of the metal. The method is then a weak charge approximation. They assume that the only effect on the ion is to polarize the crystal and do not consider the case of a moving ion, but in these limits they do calculate the force on the ion, and obtain the same result as Huntington and Grone above. Another drawback in the method is in using a definite ground state in the metal. A set of states is required for the conduction process to allow for the scattering that brings about a drift velocity. This objection may be overcome by using a density matrix formalism and in Chapter IV of this thesis we shall return to such a quantum mechanical calculation. In our analysis we shall not assume the ion to be stationary, although we shall maintain the approximations involved in considering the ionic potential as a perturbation.

All these methods ignored one or more of the following three requirements. (i) After scattering the electrons redistribute themselves and this electron density

contributes to the potential through which they were originally scattered by the Poisson equation. (ii) Experimentally the ion may move. (iii) The charge on the ion cannot be less than unity so that a perturbation method cannot be expected to yield useful results near the ion. It was with these points in mind that A.K. Das (D. Phil. 1966) turned to another method.

This analysis of the interaction force used the Boltzmann Transport equation. Das recognised the connection between the redistribution of the electrons after scattering and the correction V_1 to the potential through which they were scattered. His method then involved the Poisson equation expressing this potential in terms of the deviation of the electron density from equilibrium n_1. The second requirement was included by constructing the Boltzmann equation in the frame of the moving ion. The velocity of the ion was an arbitrary parameter. Das was able to show that the two parameters , the velocity of the ion and the external field, could be considered as one. The external field is equivalent to an electron drift velocity or an increase in the ionic velocity relative to the electron. This formalism is used in the present work. Das' own analysis of these equations, by expanding the distribution function in spherical harmonics, runs into trouble on the question of convergence. After writing his thesis Das did recognise his error, but was not able to understand this aspect. In chapter III we shall return to this method in the belief that it will be useful at short range where our own method fails. We are able to give a physical interpretation of the convergence problem and to show that the distribution function contains some sort of singularity which will require at least four harmonics.

In doing this we extend a calculation of Peierls repeated in appendix II which considers a Fourier Transform of the Boltzmann equation for weak charge on the ion. This method itself may be used to calculate the force, but the resulting logarithmic divergence may only be understood in terms of a quantum mechanical cut-off.

The quantum mechanical calculation of chapter IV considers the moving ionic potential as a perturbation on the pure metal and proceeds to a self-consistent field. This method assumes that, near the ion where quantum mechanical effects will dominate, the effect of the mean free path of the electrons is negligible. The resulting potential is considered to first order in the velocity, giving two terms. Firstly, the stationary term is identical with that given in Ziman (1964) for the k dependence of the screening parameter in the screened Coulomb potential.

$$V_0 = \frac{4\pi Z e^2}{k^2 + \alpha^2(k)} \cdot \frac{1}{(2\pi)^3}$$

Secondly, the term linear in the velocity is identical to Peierls' result in the long mean free path limit, but involves a cut-off condition. It is the success of the limit that gave us the clue to understanding the lack of convergence in the spherical harmonic expansion; it is the appearance of the cut-off in this calculation that may be used to discuss the form of the potential near the ion with which we may estimate the force.

It would be unnatural to discuss the quantum mechanics of this problem without reference to modern many-body techniques. The high density degenerate electron gas has been analysed by the method of Gell-Mann and Brueckner using the Feynman-Dyson techniques of field theory but this has not

shown anything new to our problem. Dubois (1959) has derived a similar result to our S.C.F. method. In those calculations the so-called "ring" diagrams are shown to dominate in each order of the perturbation expansion and this series summed exactly. Whilst these terms do dominate at $q \to 0$, or the weak charge limit, this cannot be demonstrated at $q \to \infty$ which dominates the behaviour at short range. This perturbation method does not, and for the same reasons as the S.C.F. method, should not give sensible results at short range.

I.iv. Our Model

We aim to derive an expression for the force by considering the potential energy at the ion due to the redistribution of the electrons after scattering. In the first instance the ionic potential is just the screened Coulomb potential of Debye and Hückel, but this exaggerates the screening at short distances. This is shown in the quantum mechanical calculation of chapter IV but is now a standard text book result. The ionic potential will be further modified by the surrounding metallic ions, but the atomic polyhedron around the ion is, in most metals, of sufficiently high symmetry for us to consider it spherical.

It is our intention to consider the velocity of the ion to be small, but not necessarily its charge. The total potential around the ion will then be $V_0 + V_1$. The first term is the potential discussed in the previous paragraph. But as the electrons scatter off this ion and it moves through the lattice there is a correction V_1 to the potential which is linear in the ionic velocity u. If as the ion moves through the crystal the screening cloud moves with it we shall have "complete dynamical screening",

and the force will be due entirely to the drift effect. We shall find that the ion is also partially screened.

The potential V_1 which will govern the motion of the electrons in the metal is related by the Poisson equation to the correction n_1 to the equilibrium electron distribution, n_0. This equilibrium distribution is the Fermi-Dirac distribution of electronsin a metal. This is itself, a solution to the Poisson equation:

$$\nabla^2 V_0 = -\alpha^2 \int n_0 d^3\underline{p} + Ze^2 \delta(\underline{r}) + e\rho_0$$

ρ_0 is the distribution of positive charge on the lattice. We construct our model so that this lattice is replaced by a uniform positive background of charge as in the jellium model of Ziman (1964). Also implied in the equation is that the electrons in a metal are a gas of independent particles. We include the exchange force associated with the anti-symmetry of the wave-functions by considering the Fermi-Dirac solution to the above equation.

Following Das we describe the transport properties by a distribution function which is the solution to a Boltzmann transport equation. There is an underlying assumption that the Fermi gas may be described by a continuum statistical transport process, but there are many other applications in the theory of excitations in solids which suggest that the Boltzmann equation is still a useful description of conduction processes in solids. The distribution function $n(\underline{r}, \underline{p}, t)$ is defined such that

$$n(\underline{r}, \underline{p}, t) \quad \frac{d^3\underline{r}\, d^3\underline{p}}{(2\pi\hbar)^3}$$

is the number of electrons in volume $d^3\underline{r}\ d^3\underline{p}$ around the phase point $(\underline{r}, \underline{p})$ at time t. At equilibrium this distribution function is:

$$n_0(\underline{r}, \underline{p}, t) = \frac{1}{\left(e^{\beta(\varepsilon - \varepsilon_F)} + 1\right)}$$

with $\beta = \frac{1}{kT}$; $\varepsilon = p^2/2m$ and ε_F is the Fermi energy.

The general form of the Boltzmann equation is:

$$\frac{\underline{p}}{m} \cdot \nabla_r n - \frac{\partial V}{\partial \underline{r}} \cdot \nabla_p n + \text{scattering terms} = 0$$

We write $n = n_0 + n_1$ and $V = V_0 + V_1$. The zero order terms then lead back to the Fermi-Dirac distribution, and we ignore second order and higher terms to write the equation:

$$\frac{\underline{p}}{m} \cdot \nabla_r n_1 - \frac{\partial V_0}{\partial \underline{r}} \cdot \nabla_p n_1 - \frac{\partial V_1}{\partial \underline{r}} \cdot \nabla_p n_0 + \text{scattering terms} = 0$$

Das showed, and we repeat this in the first appendix, that we may transform this equation into the moving frame of the ion by adding a term $-\frac{u}{\tau} p_z \partial n_0 / \partial E$. We write the scattering terms using the collision time τ of Peierls, and the final Boltzmann equation is:

$$\frac{\underline{p}}{m} \cdot \frac{\partial n_1}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}} \cdot \frac{\partial n_1}{\partial \underline{p}} - \frac{\partial V_1}{\partial \underline{r}} \cdot \frac{\partial n_0}{\partial \underline{p}} + \frac{n_1}{\tau} - \frac{\bar{n}_1}{\tau} + \frac{u}{\tau} p_z \frac{\partial n_0}{\partial E} = 0$$

with V_1 given by the Poisson equation:

$$\nabla^2 V_1 = -\alpha^2 \int n_1 \, d^3\underline{p}$$

The use of the collision parameter τ has many disadvantages. We shall find difficulties close to the ion where the collision mechanism depends on the structure of the surrounding lattice. Also the experimental results with which we shall want to compare our conclusions are dominated by two band conductors as in transition metals with a large

transition between s and d bands. In this case we cannot define a single parameter τ and this prevents us from determining a carrier velocity u_E .

In the next chapter we derive an expression for the long-range solution to the Boltzmann equation. The Boltzmann equation in the frame of theion is written in terms of an operator B, the correction n_1 to the equilibrium distribution function n_0 , and three terms S such that $B n_1 = S$. The first source term $S_1 \propto u \beta_z$ is due to the transformation into the frame of the ion. The second source term $S_2 = \bar{n}_1/\tau$ is just the scattering in term due to the mean distribution at any point. The final term $S_3 \propto \frac{\partial V_1}{\partial z}$ is related to the change in electrostatic potential of the ion arising from the redistribution of the electrons after scattering. We find that we may factorize $\frac{\partial n_0}{\partial E}$ from the distribution function. We proceed to derive an expression for the Green's function of the operator B satisfying:

$$B(\underline{r}, \underline{p})\, G(\underline{r}, \underline{p}; \underline{r}', \underline{p}') = \delta(\underline{r}-\underline{r}')\,\delta(\underline{p}-\underline{p}')$$

We are able to convert the differential Boltzmann equation into the integral equation:

$$n_1(\underline{r}, \underline{p}) = \iint d^3\underline{r}'\, d^3\underline{p}'\; G(\underline{r}, \underline{p}; \underline{r}', \underline{p}')\, S(\underline{r}', \underline{p}')$$

The integration is evaluated as a sum over a family of orbits, but we find a complex orbit structure. We find that the Green's function has to be divided into two parts, one for orbits passing through the scattering region G_1 , and the other, for the straight line orbits, G_0 for the pure metal. These functions are separately calculated and we find that the integral equation $\bar{n}_1 = \int G_0 S + \int G_1 S$ may be simply transformed into momentum space. $\int G_0 S$ is

a convolution in coordinate space, and $G_1(r, r')$ factorizes to $G_1'(r)\ G_1''(r')$; both these forms are transformed, and the solution calculated.

This method does not have the disadvantage of the methods discussed in section I.iii. We include the correction V_1 to the potential arising from the redistribution of electrons after scattering, but express the result in terms of the transport cross-section of the stationary potential V_0 . We have not made any approximation about the charge strength on the ion and have made allowance for the ion to move.

The limitations are all related to the behaviour of the functions near the ion. We have already mentioned the problems of representing the background scattering by a collision time in this region. We also make the approximation that all scattered orbits pass through the scattering centre itself so that the Green's function G_1 factorizes. We do not consider details of the orbits inside the scattering region as these are only fit for extensive numerical computation. The result of these approximations is that we have to consider a cut-off in the distribution function so derived. We discuss methods that may lead to an understanding of its behaviour inside the scattering region in Chapters III and IV and finally give an estimate in Chapter V of the force, based on a discussion of the cut-off mechanism. The magnitude of this force suggests that it may well be sufficient to lead to the effects discussed earlier but cannot easily be compared.

The drift force is, apart from constants, just as would be obtained from a 'dimensional' argument.

$$F_{drift} = -Z^2 eE \frac{l}{a}\left[\frac{1}{12\pi} + \frac{\frac{\alpha^2 Q}{6\pi e'}}{1+\frac{\alpha^2 Q}{6\pi e'}}\,\frac{\alpha^2 Q}{15 e' Z^2}\right]$$

Z: charge on the ion; e': the exponential root; α: inverse screening radius; Q: transport cross-section ($Q \sim z^2$).

The second term we obtain is not so easily understood. Following the argument of section II it would appear to be a screening force, but it may become larger than the direct field force:

$$F_{field} + F_{screening} = ZeE\left[1 - \frac{\frac{\alpha^2 Q}{6\pi e'}}{1+\frac{\alpha^2 Q}{6\pi e'}}\,\frac{l}{a}\right]$$

We conclude that the interpretation as a screening force may not be correct, but we can see no other mechanism, or that the Green's function method exaggerates this term, in which case we propose a further calculation. We suggest that the total current may yield more information. We find no contradiction with experiment, but are not able to compare the results in detail.

CHAPTER II

II.i The Approach to the Force

There are two parameters in the drift force: the ion velocity u and external field E. In this analysis we show that they may be described by a single parameter which is the velocity of the ion relative to the electron gas. The electric field will then have been replaced by the drift velocity of the electrons. We consider the case where the "effective" ion velocity is small and expand the distribution function $n(r, p)$ to first order in this parameter $n = n_0 + n_1$ The stationary distribution function n_0 is the Fermi-Dirac function describing the electron distribution in a metal

$$n_0 = \left[\exp (E - E_F)/kT + 1\right]^{-1} \qquad (II.i.1)$$

We propose to derive an expression for n_1, linear in the velocity u by solving a Boltzmann transport equation and to use this to obtain the force. The electron density, the momentum integral of this function, is related to an

electrostatic potential φ_1 through the Poisson equation and this must be added to the stationary ion potential φ_0 to give the potential in the transport equation. For convenience we shall use the potential energy $V = V_0 + V_1 = e\varphi_0 + e\varphi_1$ instead of the electrostatic potential $\varphi_0 + \varphi_1$.

V_0 is the solution to the Thomas-Fermi equation:

$$\nabla^2 V_0 = -4\pi e^2 \left\{ \frac{1}{3\pi^2\hbar^3} \left[2m\left(E_F - V_0(r)\right) \right]^{3/2} - \rho_0 \right\} \qquad (\text{II}.i.2)$$

where ρ_0 is the positive background charge density. In the limit of weak charge on the ion this potential takes the form of the classical screened Coulomb potential of Debye and Hückel.

$$V_0\Big|_{Z\to 0} = Ze^2 \frac{e^{-\alpha r}}{r} \qquad (\text{II}.i.3)$$

The full solution depends on the relative magnitude of the Fermi energy E_F and the potential V_0. All we need to know is that the potential is bounded by a screening radius a such that:

$$V_0 \sim \begin{cases} \dfrac{Ze^2}{r} & r < a \\ \text{negligible} & r > a \end{cases} \qquad (\text{II}.i.4)$$

We look for the solution to the Boltzmann and Poisson equations for n_1 and V_1 by transforming them into a single integral equation and much of this chapter is concerned with deriving the kernel or Green's function of that integral equation. The force on the ion is simply related to the velocity dependent potential. If we define the direction of motion of the ion to be the z-axis of a Cartesian coordinate system then the force is given by:

$$F = Z \frac{\partial V_1}{\partial z}\Big|_{r\to 0} \qquad (\text{II}.i.5)$$

In making n_1 the subject of the integral equation we shall everywhere want to express V_1 as a function of n_1 and in this first section we shall solve the Poisson equation for this expression. We shall also consider another formulation of the force which is attractive in suggesting a solution using the Liouville theorem of statistical physics but which turns out to be intractable.

Before considering these formulations of the force we may deduce some properties of the function n_1 from the symmetry of the Boltzmann equation. In the moving frame of the ion this equation takes the form derived by Das:

$$\frac{\underline{p}}{m}\cdot\frac{\partial n_1}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}}\cdot\frac{\partial n_1}{\partial \underline{p}} - \frac{\partial V_1}{\partial \underline{r}}\cdot\frac{\partial n_0}{\partial \underline{p}} + \frac{1}{\tau}(n_1-\bar{n}_1) + \frac{u}{\tau}p_z\frac{\partial n_0}{\partial E} = \frac{dn_1}{dt} = 0 \qquad (II.i.6)$$

for the stationary solution $n_1(\underline{r},\underline{p})$. In this expression $\bar{n}_1$ is the angular average of n_1:

$$\bar{n}_1(\underline{r},p) = \int n_1(\underline{r},\underline{p})\,\frac{d\omega_p}{4\pi} \qquad (II.i.7)$$

The electron density is then given by:

$$\int n_1\, d^3\underline{p} = 4\pi\int \bar{n}_1\, p^2\, dp \qquad (II.i.8)$$

and this function is related to V_1 through the Poisson equation. Now all the terms in the transport equation (II.i.6) may be expressed as derivatives or integrals of the function n_1 except for the term in p_z. Furthermore all these terms are invariant under a rotation of $\underline{r}$ and $\underline{p}$ whereas the p_z term transforms as a vector. This requires that n_1 too must transform as a vector and will take the general form:

$$n_1(\underline{r},\underline{p}) = \frac{\underline{r}}{r}\,f(r,p,\cos\theta) + \frac{\underline{p}}{p}\,g(r,p,\cos\theta) \qquad (II.i.9)$$

where θ is the angle between $\underline{r}$ and $\underline{p}$, or $\cos\theta = \underline{r}.\underline{p}/rp$ Now $\bar{n}_1$ will contain a factor z. We shall also find that we may factorize $\partial n_0/\partial E$ from this mean distribution function. In a metal the electron gas may be considered at zero temperature in which case the derivative of the Fermi-function is a delta-function at the Fermi energy E_F. We may define a function $\bar{f}(\underline{r})$:

$$\bar{n}_1(\underline{r},p) = \bar{f}(\underline{r})\frac{\partial n_0}{\partial E} = \frac{m}{p_F}\frac{\partial n_0}{\partial p}\bar{f}(\underline{r}) \qquad (\text{II}.\text{i}.10)$$

and, using the symmetry of n_1, define a function $\nu(r)$:

$$\bar{f}(\underline{r}) = \nu(r)\,z \qquad (\text{II}.\text{i}.11)$$

so that the electron density is given by:

$$\int n_1 d^3p = 4\pi\int \bar{n}_1 p^2 dp = 4\pi\int \bar{f}(\underline{r})\frac{\partial n_0}{\partial E}p^2 dp = 4\pi m p_F \nu(r) z \qquad (\text{II}.\text{i}.12)$$

When we solve the Poisson equation for the potential V_1 with this form for the distribution function then V_1 too may be factorized and we define a function $\mu(r)$:

$$V_1(\underline{r}) = \mu(r)\,z \qquad (\text{II}.\text{i}.13)$$

From the form of the Boltzmann equation in the frame of the ion (equation II.i.6), we are able to demonstrate the equivalence between the external field E and the electron drift velocity u_E in forming the effective ion velocity as a single parameter. We consider the terms in V_1 and u. If we apply the external electric field then $\partial V_1/\partial\underline{r}$ is everywhere replaced by $\partial V_1/\partial\underline{r} + \underline{E}$; if we add the drift velocity u_E the ionic velocity is $(u_0 + u_E)$. We assume the material to be isotropic and the drift velocity to be collinear with the field so that the third and fifth terms of equation (II.i.6) are

written:

$$\left(\frac{\partial V_1}{\partial r} + \underline{E}\right)\cdot\frac{\partial n_0}{\partial \underline{p}} + (u_0 + u_E)\frac{m}{\tau p}p_z\frac{\partial n_0}{\partial p} \equiv \frac{\partial V_1}{\partial r}\cdot\frac{\partial n_0}{\partial \underline{p}} + u_0\frac{m}{\tau}\frac{p_z}{p}\frac{\partial n_0}{\partial p}$$

If $u_E = -\frac{e\tau}{m}E$ then these terms have the same form as II.i.6. This invariance of the Boltzmann equation enables us to put the boundary condition on the potential as $\mu(r \to \infty) = 0$ provided we use the effective ion velocity

$$u = u_0 - \frac{e\tau}{m}E \qquad \text{(II.i.14)}$$

We note that this model is not applicable to a two-band conductor because the velocity u_E depends on the mean free path of the carriers. If there are two types of carrier, we cannot define this velocity uniquely.

But the more serious drawback even in the single band conductor comes from the concept of a constant collision time applied near the ion. This concept requires a uniform positive background and uniform distribution of all scattering centres so that a collision may occur at any point. Whilst being a useful model at large distances from the ion, it will break down near the ion where this background will have a definite structure.

We might try and extend the concept by deriving a velocity dependence of the collision time. Close to the ion the higher electron velocity would change the collision probability. To accommodate this effect we would need to discuss the lattic dynamics in a collision near the ion. This is beyond the scope of this thesis and we have to make reservations about the validity of our solution near the ion.

We are now able to solve the Poisson equation for μ in terms of ν . Using equation (II.i.12):

$$\nabla^2 V_1 = -\frac{8\pi e^2}{\hbar^3} 4\pi m p_F \nu(r) r\cos\theta = -\alpha^2 \nu(r) r\cos\theta \qquad \text{(II.i.15)}$$

The parameter α is defined by $\alpha^2 = 32\pi^2 e^2 m p_F/\hbar^3$
This is the classical screening parameter. In terms of μz :

$$\nabla^2 V_1 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r} r\mu\cos\theta\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial}{\partial r} r\mu\cos\theta\right)$$

$$= \frac{\cos\theta}{r^2}\frac{d}{dr}\left(r^4 \frac{d\mu}{dr}\right) \qquad \text{(II.i.16)}$$

From (II.i.15) and (II.i.16):

$$\frac{d\mu}{dr} = -\frac{\alpha^2}{r^4}\int_0^r \nu(r') r'^4 dr' \qquad \text{(II.i.17)}$$

where we have used the boundary condition that $\frac{d\mu}{dr}$ vanish at the origin. Using the boundary condition $\mu(\infty) = 0$

$$\mu(r) = -\alpha^2 \int_r^\infty \frac{dr'}{r'^4}\int_0^{r'} dr'' r''^4 \nu(r'')$$

This integral may be simplified by changing the order of integration:

$$\left.\begin{array}{l} 0 < r'' < r' \\ r < r' < \infty \end{array}\right\} \Rightarrow \left.\begin{array}{l} r < r' < \infty \\ 0 < r'' < r \end{array}\right\} + \left.\begin{array}{l} r'' < r' < \infty \\ r < r'' < \infty \end{array}\right\}$$

$$\mu(r) = -\alpha^2\left\{\int_0^r dr'' r''^4 \nu(r'')\int_r^\infty \frac{dr'}{r'^4} + \int_r^\infty dr'' r''^4 \nu(r'')\int_{r''}^\infty \frac{dr'}{r'^4}\right\}$$

$$\boxed{\mu(r) = -\frac{\alpha^2}{3}\left\{\frac{1}{r^3}\int_0^r dr' r'^4 \nu(r') + \int_r^\infty dr' r' \nu(r')\right\}} \qquad \text{(II.i.18)}$$

The force is then:

$$F = Z\frac{\partial}{\partial z}(\mu z)\Big|_{r=0} = Z\left\{\mu(0) + \frac{z^2}{r}\frac{\partial \mu}{\partial r}\Big|_{r=0}\right\} = \mu(0)Z$$

$$\boxed{F = -Z\frac{\alpha^2}{3}\int_0^\infty dr'\, r'\, \nu(r')} \qquad (\text{II.i.19})$$

We may obtain an alternative expression for the force by considering the rate of change of the total electron momentum. We integrate the product $p_z\, \partial n_1/\partial t$ over all phase space and choose the equilibrium condition that this quantity is zero to express the force on the ion in terms of a distribution function φ which is simply related to n_1.

From Das' form of the Boltzmann equation in the frame of the ion (equation II.i.6) the rate of change of the total electron momentum is given by:

$$\frac{\partial P_z}{\partial t} = \int d^3\underline{p}\, p_z \frac{\partial n_1}{\partial t} = \frac{1}{m}\int d^3\underline{p}\, p_z \underline{p}\cdot\frac{\partial n_1}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}}\cdot\int d^3\underline{p}\, p_z \frac{\partial n_1}{\partial \underline{p}} - \frac{\partial V_1}{\partial \underline{r}}\cdot\int d^3\underline{p}\, p_z \frac{\partial n_0}{\partial \underline{p}}$$

$$+ \int d^3\underline{p}\, \frac{p_z}{\tau}(n_1 - \bar{n}_1) + \int d^3\underline{p}\, \frac{u}{\tau} p_z^2 \frac{\partial n_0}{\partial E} \qquad (\text{II.i.20})$$

The second and third terms of this expression may be written in terms of the electron density to first and second order for:

$$\int p_z \frac{\partial n_{0,1}}{\partial \underline{p}}\, d^3\underline{p} = -\frac{\underline{p}_z}{\underline{\ }} \int n_{0,1}\, d^3\underline{p}$$

using the boundary conditions at infinity that $n_{0,1} = 0$ ($\hat{p}_z$ is a unit vector in p_z direction). The Poisson equations for n_0 and n_1 are, with $\beta = \alpha^2/4\pi m p_F$:

$$\int n_0 d^3p = -\frac{1}{\beta}\nabla^2 V_0 + \frac{Ze^2}{\beta}\delta(r)$$

$$\int n_1 d^3p = -\frac{1}{\beta}\nabla^2 V_1 \qquad \text{(II. i.21)}$$

With these expressions:

$$\frac{\partial V_0}{\partial r}\cdot\int p_z \frac{\partial n_1}{\partial p} d^3p + \frac{\partial V_1}{\partial r}\cdot\int p_z \frac{\partial n_0}{\partial p} d^3p$$

$$= \frac{1}{\beta}\frac{\partial V_0}{\partial z}\nabla^2 V_1 + \frac{1}{\beta}\frac{\partial V_1}{\partial z}\nabla^2 V_0 - \frac{Ze^2}{\beta}\delta(r)\frac{\partial V_1}{\partial z} = \frac{1}{\beta}\left[\nabla(\nabla V_0\cdot\nabla V_1)\right]_z - \frac{Ze^2}{\beta}\delta(r)\frac{\partial V_1}{\partial z}$$

If the ion were not present, the Boltzmann equation would reduce to:

$$\frac{1}{\tau}(n_1^\circ - \bar{n}_1^\circ) = -\frac{1}{\tau}u p_z \frac{\partial n_0}{\partial E}$$

which has the solution $n_1^\circ = -u p_z \frac{\partial n_0}{\partial E}$ (II.i.22)
This is the change in density arising from the transformation into a frame moving with velocity u relative to the electron gas. We now replace the ion and define a function $\varphi(r, p)$ as that term in n_1 which is due to the presence of the ion rather than to the change of reference frame:

$$n_1 = n_1^\circ + \varphi$$

The fourth and fifth terms of (II.i.20) are simplified using

$$\int d^3\underline{p}\; p_z\, \bar{\Phi} = 0$$

$$\int d^3\underline{p}\; \frac{p_z}{\tau}\left(n_1 - \bar{n}_1 + u p_z \frac{\partial n_0}{\partial E}\right) = \int d^3\underline{p}\; \frac{p_z}{\tau}\,\Phi$$

Adding terms we have:

$$\frac{\partial p_z}{\partial t} = \frac{1}{m}\int d^3\underline{p}\, p_z \underline{p}\cdot\frac{\partial n_1}{\partial \underline{r}} - \frac{1}{\beta}\left[\nabla\left(\nabla V_0 \cdot \nabla V_1\right)\right]_z + \frac{Ze^2}{\beta}\frac{\partial V_1}{\partial z}\delta(\underline{r}) + \frac{1}{\tau}\int p_z \Phi\, d^3\underline{p}$$

Integrating over all coordinate space with boundary at infinity the term in $\nabla(\nabla V_0 \cdot \nabla V_1)$ vanishes and:

$$\int d^3\underline{r}\,\frac{\partial p_z}{\partial t} = \int d^3\underline{r}\,\frac{1}{m}\frac{\partial}{\partial \underline{r}}\cdot\int \underline{p}\, p_z\, n_1 d^3\underline{p} + \frac{Ze^2}{\beta}\left(\frac{\partial V_1}{\partial z}\right)_{r=0} + \frac{1}{\tau}\int p_z \Phi\, d^3\underline{r}\, d^3\underline{p} \qquad (\text{II.i.23})$$

The first term may be written as the surface integral:

$$\int_S d\sigma\; \underline{n}\cdot\int \underline{p}\, p_z\, n_1 d^3\underline{p}$$

where $\underline{n}$ is the outward normal vector to the surface S which is taken in the limit to infinity. The p_x and p_y components of the $\underline{p}$ integration trivially vanishes:

$$\underset{r\to\infty}{\text{Lt.}} \int_{-\pi}^{\pi} p_x\, d\phi_x = 0$$

But in the case of p_z the surface integral is important and the limit has to be taken carefully. We showed in equation (II.i.9) that n_1 may have a dipole term in z. The p - integrand may then vary as $p_z^2\,\frac{z}{r^3}$. The p integration will then not necessarily vanish and we may be left with a surface integral of the form

$$\int_S d\sigma\; n_z\,\frac{z}{r^3}$$

This integral depends on the shape and not on the

size of the surface S . It will vanish in the limit only if the extension in the z direction is large compared with that at right angles. For example, for a cylinder of length $2L$ and radius R the contributions to the integral comes from the end faces, and is:

$$1 - \frac{L}{\sqrt{L^2 - R^2}}$$

This function vanishes in the limit $L \to \infty$ and $R \to \infty$ if $L >> R$ and tends to 1 if $R \gg L$. It is then necessary in considering the $p_z \varphi$ integration to consider a volume V having this cylindrical shape and integrate over the space with $z >> x, y$. (This is similar to the hydrodynamic case of the momentum of the liquid surrounding a moving body.) We do not use this result in the present chapter, for the reasons we shall give, but return to it briefly in Chapter V.

In this limit, $r \to \infty$, and in steady state conditions ~~equation (II.i.23)~~ $\frac{\partial p_z}{\partial t} = 0$

$$Z \left(\frac{\partial V_1}{\partial z}\right)_{r \to 0} = - \frac{\alpha^2}{4\pi e^2 m p_F t} \int d^3 r \, d^3 p \, p_z \varphi$$

The term on the left is the force on the ion. We see how it may be formulated in terms of the function φ . In this chapter we shall show that for electrons directed towards the scattering region $n_1(r, p)$ is just n_1^0 and $\varphi = 0$. In this region "upstream" from the ion the electrons are unaware of the impending collision and distribute themselves as though the ion were not present. It is the scattering from the ion that disrupts this spatial uniformity downstream where, in general, $\varphi \neq 0$. We are tempted to invoke a simple theorem. In statistical physics the equation of motion of the distribution function in phase space derives from the equation of continuity and is known as

Liouville's theorem. An important consequence of this theorem is that in a closed system the distribution function is constant along a path in phase space. We may treat our electron gas as a closed system. We have shown how the external field may be replaced by an ion velocity u_E. The "scattering-in" arising from the interactions with the lattice or positive background is a source of new electrons. These electrons travel along an orbit and finally scatter out of the system. So instead of considering the entire orbit with sources and sinks we only consider a small section of it. We do this by introducing an exponential factor to the entire orbit. On this model we may apply Liouville's theorem to show that n_1 must be the same at any point on the path upstream as it is downstream.

The difficulty in using this property of the distribution function arises when we try to connect the paths across the scattering centre. Although the Green's function method does in principle follow the paths in phase space we find that we are only able to approximate the orbits inside the scattering region. We are only able to calculate the average distribution function, and even that only outside the scattering radius.

II.ii The Integral Form of the Boltzmann Equation

In this section we describe the motion of the electrons in terms of their orbits and introduce the formalism of the Green's function approach that is developed in the next three sections. We write the differential Boltzmann equation as an integral equation by defining the Green's function $G(\underline{r}, \underline{p}\,;\, \underline{r}', \underline{p}')$. The integral equation then takes the form of a product of the Green's function and source

terms S summed over a family of orbits. We find a complex orbit structure in which some orbits are straight and some scattered and this is simplified by dividing the Green's function into G_0 and G_1 . The product $G_0 S$ is summed over all the straight line orbits including those that originate in the shadow of the ion; the product $G_1 S$ is summed over all orbits that pass through the scattering region. The scattered orbits are described in terms of the complete Green's function and each of these is paired with a straight line orbit originating in the shadow of the ion which should have been deducted from the $G_0 S$ integration. We may then write $G_1 = G - G_0$. The use of this formalism will become apparent in later sections. We find in section II.v. that $G_0 S$ is a convolution in coordinate space when summed over all possible and impossible straight line orbits. This may be Fourier transformed into a simple product. We also find, in sections vi, vii, and viii, that the straight line shadow orbits subtract terms which are similar to those from the GS scattered orbits and as a result of taking the orbits in pairs the $G_1 S$ contribution contains a factor equal to the transport cross-section.

We consider the Boltzmann equation in the region outside the screening radius of the classical theory. In factorizing $\partial n_0 / \partial E$ from the distribution function $\bar{n}$, the electron energy may be replaced by the Fermi energy. In the region outside the scattering radius the screened potential is so small that we may ignore its correction to the kinetic energy and replace the electron momentum by its asymptotic value: $p^2 = p_F^2$. We may now describe the motion of the electrons in terms of their orbits. Outside the scattering region these are straight. Inside the scattering region we approximate the orbits by extrapolating the straight paths to the ionic origin. This model allows us to connect the orbits

across the scattering region but it introduces a singularity in the distribution function as a result of the confluence of orbits at the ion. We shall often be reminded of this situation in the calculation and its justification can only lie in the validity of the approximation at long range. The model might well be extended to consider more realistic orbits but is then likely to involve extensive numerical calculation.

With this form of the orbit we investigate the electron density by considering the transport equation in a medium of uniform positive charge. We include the effect of collisions with other electrons, impurities, or lattice defects, by a collision parameter τ . Using the Boltzmann equation in the frame of the ion (equation II.i.6) we derive a Green's function for the equivalent homogeneous equation. The Green's function is the probability that an electron leaving one point on an orbit will arrive at another point on the same orbit without being scattered off. The inhomogeneous equation has three source terms: one is due to the velocity of the ion, the second represents the "scattered-in" electrons and is proportional to the mean distribution function $\bar{n}_1$, and the third arises from the first order correction V_1 to the potential. The technique is to take the productof the Green's function with the source terms at a point, and sum the contributions at the final point to obtain the electron distribution function.

We write the equivalent homogeneous Boltzmann operator B and the source terms S . The Boltzmann equation is then:

$$B(r,p)\, n_1(r,p) = S(r,p) \qquad \text{(II.ii.1)}$$

with

$$S(\underline{r},\underline{p}) = -\frac{um}{\tau p} p_z \frac{\partial n_0}{\partial p} + \frac{\bar{n}_1}{\tau} + \frac{\partial V_1}{\partial \underline{r}} \cdot \frac{\underline{p}}{p} \frac{\partial n_0}{\partial p} \qquad (\text{II.ii.2})$$

The Poisson equation for V_1 is:

$$\nabla^2 V_1 = -4\pi e^2 \int n_1 \, d^3\underline{p} \qquad (\text{II.ii.3})$$

The Green's function satisfies the equation:

$$B(\underline{r},\underline{p})\, G(\underline{r},\underline{p};\underline{r}'\underline{p}') = \delta(\underline{r}-\underline{r}')\,\delta(\underline{p}-\underline{p}') \qquad (\text{II.ii.4})$$

with which we are able to convert the differential Boltzmann equation into the integral equation:

$$n_1(\underline{r},\underline{p}) = \iint d^3\underline{r}'\, d^3\underline{p}'\; G(\underline{r},\underline{p};\underline{r}',\underline{p}')\; S(\underline{r}',\underline{p}') \qquad (\text{II.ii.5})$$

This equation takes on greater complexity when we consider the orbit model in detail. We may consider the integration over the phase variables $(\underline{r}', \underline{p}')$ as a summation over a family of orbits. The equation of motion may be used to show that in general there are no orbits passing through the two phase points $(\underline{r}, \underline{p})$ and $(\underline{r}', \underline{p}')$ but with our model, which considers a small scattering region, there are two orbits which pass through the points $\underline{r}$ and $\underline{r}'$ of coordinate space. For most values of $\underline{r}$ and $\underline{r}'$ one of these orbits passes through the scattering region, and the other is the straight line path between $\underline{r}$ and $\underline{r}'$ as shown in Figure II.i.

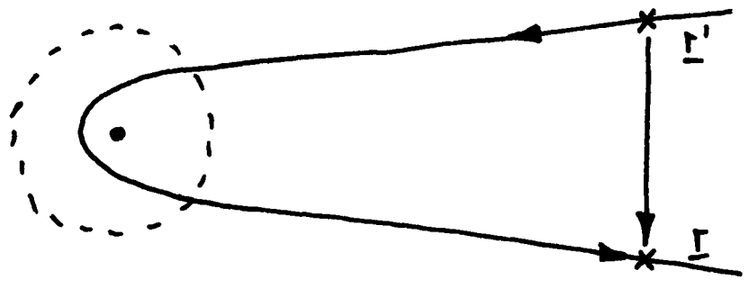


Fig. II.1

For those points $\underline{r}'$ which, relative to $\underline{r}$, lie in the shadow of the scattering region there are two scattered orbits and no straight ones, as in figure II.2.

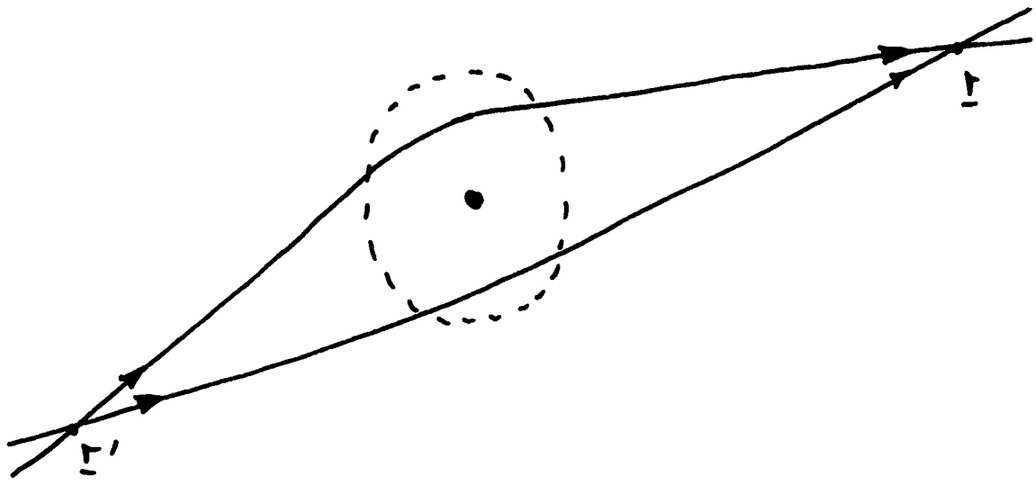


Fig. II.2

We may represent this orbit structure graphically with reference to the angles defined in figures II.3a and b.

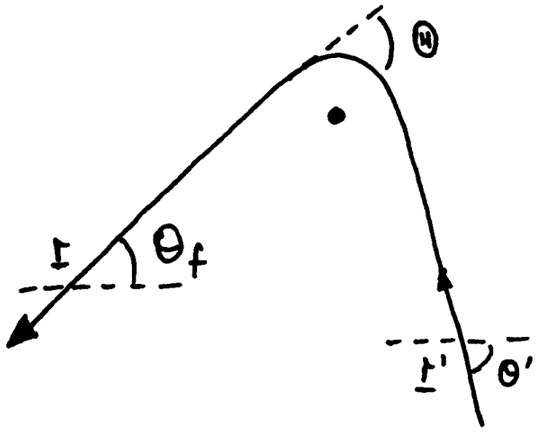


Fig II.3a

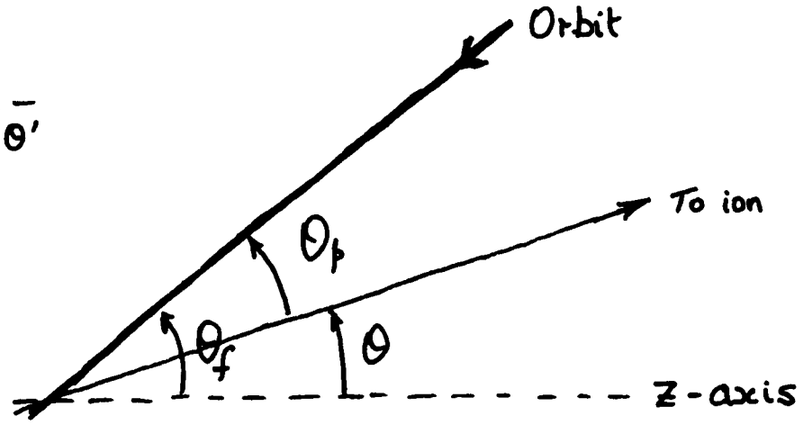


Fig II.3b

Consider first that r is close to the z-axis through the ion as in Figure II.4. If the potential has a sharp cut-off at $r = a$ then $\theta_f = \theta_p$ and $\theta_p = \theta'$ for $\theta_p > \sin^{-1}(a/r)$. As θ_p decreases we come to a value for which $\theta' = 0$ and as θ_p approaches zero, θ' increases to π.

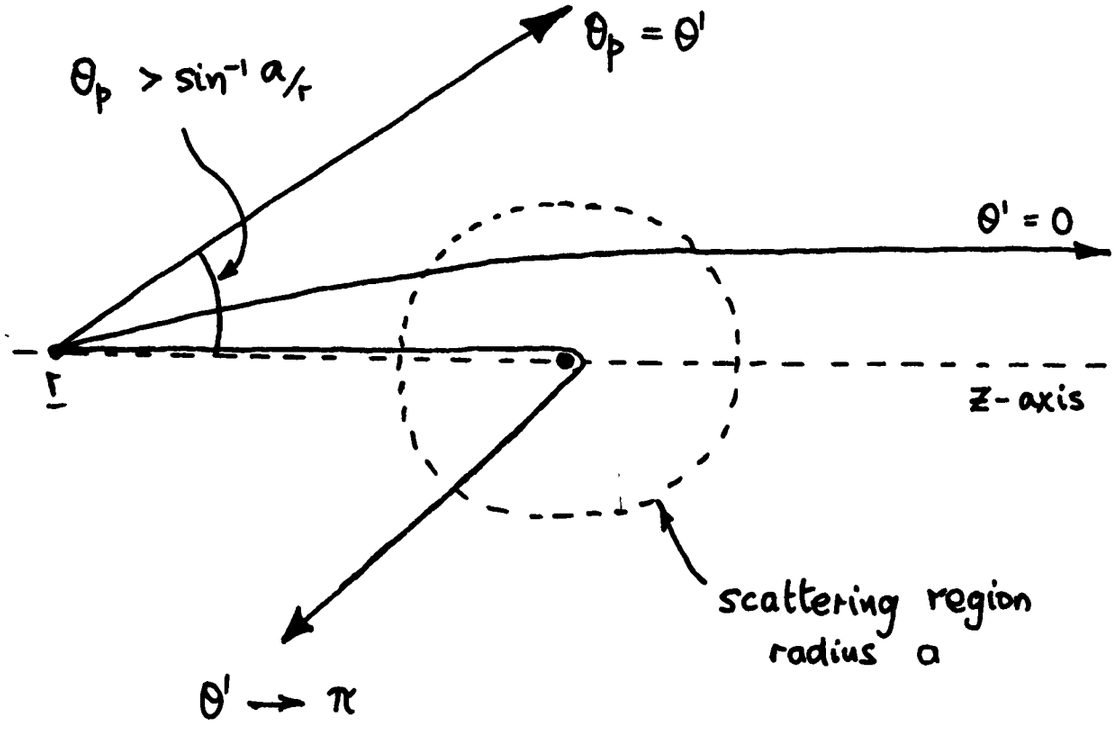


Fig. II.4

We show θ' as a function of θ_p graphically in Figure II.5

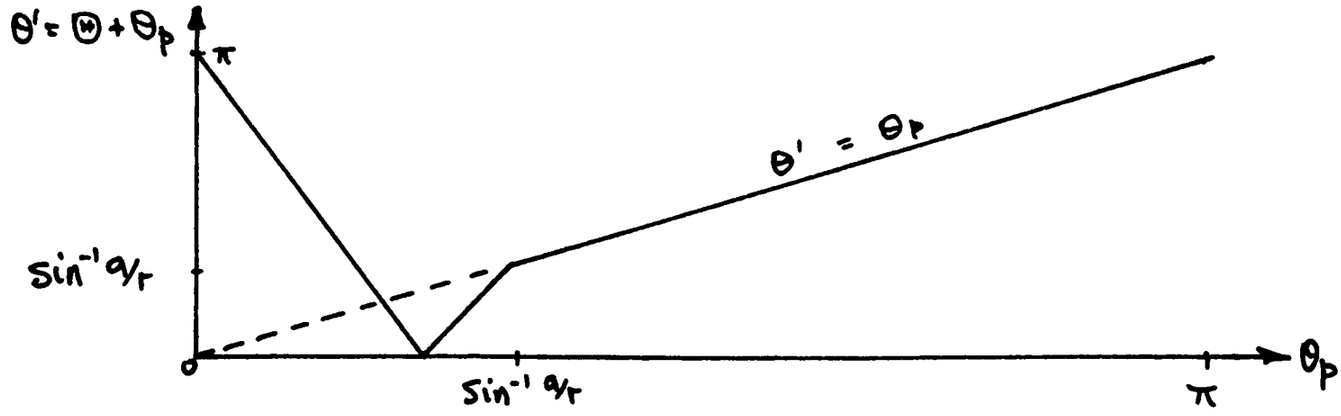


fig. II.5

We can now see that for any value of θ' there are two values of θ_p . In the region $\theta' > \sin^{-1} a/r$ there is one scattered and one straight orbit; for $\theta' < \sin^{-1} a/r$ there are two scattered orbits. A similar structure is demonstrated if we consider θ' as a function of the impact parameter b $(= r \tan \theta_p)$ for constant r , and this is shown in Figure II.6 If r is at an angle θ to the z -axis we replace θ_p of the previous discussion by $\theta_f = \theta - \theta_p$. But we shall find that we cannot handle the details of the orbit inside the

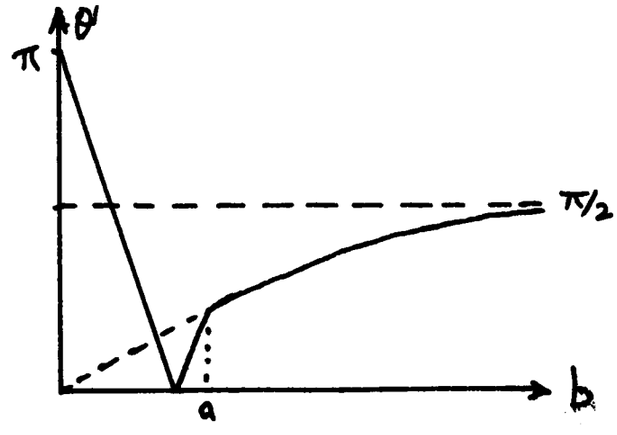


Fig. II.6

scattering region and make the approximation that all scattered orbits pass through the scattering centre itself, in which case $\theta_f = \theta$.

The way we deal with this complexity of orbits is to consider the Green's function in two parts: G_0 and G_1 The first, G_0 , is the Green's function for the straight line orbits from r' to r . We have to subtract orbits in which r' lies in the shadow of the scattering region, but it is more convenient to deduct these from the second part of the Green's function. In constructing the function G_1 we note that as all orbits are in principle scattered by the ion we may only write G_1 in the form $G - G_0$ where G

relates to all those orbits scattered by the ion through $\underline{r}$ and G_o relates to those "shadow" orbits which should have been deducted from the first Green's function. These functions satisfy the equivalent homogeneous Boltzmann equations with and without the ionic potential V_o :

$$\frac{\underline{p}}{m} \cdot \frac{\partial G_o}{\partial \underline{r}} + \frac{G_o}{\tau} = \delta(\underline{r}-\underline{r}')\,\delta(\underline{p}-\underline{p}') \qquad (\text{II.ii.6})$$

$$\frac{\underline{p}}{m} \cdot \frac{\partial G}{\partial \underline{r}} - \frac{\partial V_o}{\partial \underline{r}} \cdot \frac{\partial G}{\partial \underline{p}} + \frac{G}{\tau} = \delta(\underline{r}-\underline{r}')\,\delta(\underline{p}-\underline{p}') \qquad (\text{II.ii.7})$$

with $G_1 = G - G_o$

$$n_1(\underline{r},\underline{p}) = \iint d^3\underline{r}'\, d^3\underline{p}'\; S(\underline{r}',\underline{p}')\left[G_o(\underline{r},\underline{p};\underline{r}',\underline{p}') + G_1(\underline{r},\underline{p};\underline{r}',\underline{p}')\right] \qquad (\text{II.ii.8})$$

We have now effectively introduced three orbits into the G_1 integration for at any one θ' there are three values of θ . These correspond to two scattered orbits with positive contribution and one straight line orbit with negative contribution. The three orbits are shown in Figure II.7. We are, however, considering the θ' integral at constant θ , or constant b and we may sum the orbits in pairs as shown in Figure II.8.

Fig. II.7

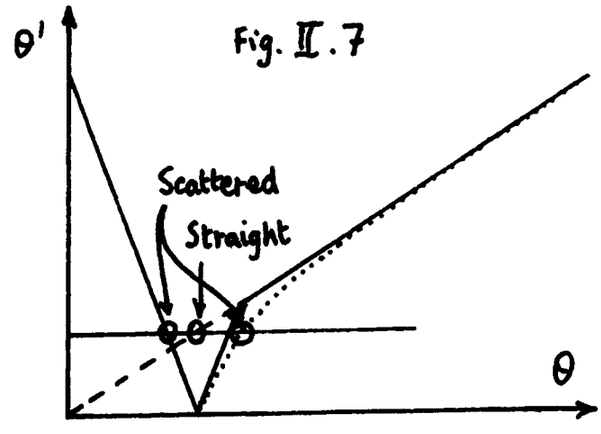
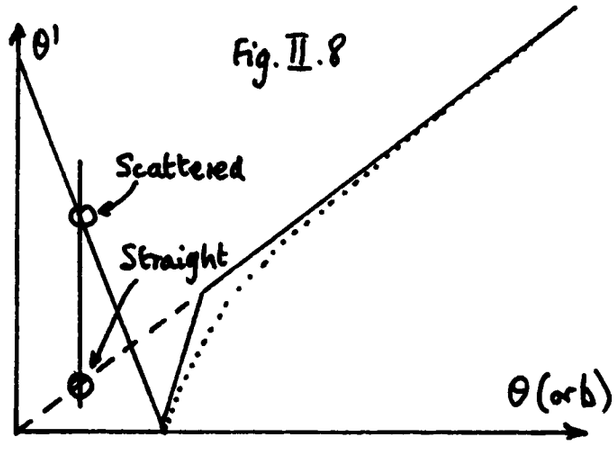


Fig. II.8



In both the figures the dotted curve shows more detail of the orbit where outside the scattering region the potential V_0 only goes asymptotically to zero so that one of the orbits is scattered for all values of Θ. Without the cut-off at $b = a$ we would integrate θ' up to π and there would always be two values of θ' for any value of θ corresponding to $\theta' = \theta$ (or $\omega = 0$) and $\theta' = \theta + \omega$. These two orbits correspond to one scattered G type and one unscattered G_0 type with $\omega = 0$. On integrating the product of the source and $(G - G_0)$ over the polar angle Φ we obtain a factor $\cos\Theta\,(1 - \cos\omega)$ which in detail gives the transport cross-section defined by:

$$Q = \int \frac{d\sigma}{d\omega}\,(1 - \cos\Theta)\,d\omega' = \int b\,db\,(1 - \cos\theta) \qquad (II.ii.9)$$

In the next section (II.iii) we derive an expression for G_0 and show that in an essentially irreversible process the Green's function is reversible. This is a result of the equivalence between the orbit from $\underline{r}$ to $\underline{r}'$ and from $\underline{r}'$ to $\underline{r}$ provided the sense of the random scattering is reversed. We derive the expression for the reversed Green's function and use it in the following section (II.iv) to calculate the momentum integrated Green's function for scattered orbits, denoted $H(\underline{r}, \underline{r}')$:

$$H(\underline{r}, \underline{r}') = \frac{1}{4\pi} \int G(\underline{r}, \underline{p}\,;\, \underline{r}', \underline{p}')\,d^3\underline{p}'\,d\omega_p \qquad (II.ii.10)$$

The p dependence in H is not shown explicitly for all functions are multiplied by $\partial n_0/\partial E$ and we may write $p = p_F$. In deriving an expression for $H(\underline{r}, \underline{r}')$ we take advantage of that aspect of our model by which all scattered

orbits pass through the ionic origin for then the function H factorizes:

$$H(\underline{r},\underline{r}') = \frac{e^{-r/l}}{4\pi r^2} \quad \frac{e^{-r'/l}}{r'^2} \quad \frac{\partial\sigma}{\partial\omega} \quad \frac{m}{p_F} \qquad (II.ii.11)$$

In section II.v. we obtain an expression for G_0 and for the Fourier Transform of the integrated product $G_0 S$. This result is left until the last section and in sectionsvi, vii and viii we calculate the contributions from the sources S_1 , S_2 and S_3 on the scattered orbits using the results of sections iii, iv and v. These are summed in section ix where we find that we may factorize the $G_1 S$ terms in the integral equation. This is directly related to the factorization of the momentum integrated Green's function H of section iv. It is then straightforward to complete the Fourier transformed integral equation and to solve the resulting algebraic equation for the transform $\bar{g}(\underline{k})$ of the mean distribution function $\bar{f}(\underline{r})$:

$$\bar{g}(\underline{k}) = \int d^3\underline{r} \; \bar{f}(\underline{r}) \; e^{i\underline{k}.\underline{r}} \qquad (II.ii.12)$$

The inverse transform is evaluated and this displays a z/r^3 singularity at the origin. We recognise that our approximations are such that we cannot use this result at short range and we leave the expression for $\bar{g}(\underline{k})$ until we can understand more about its behaviour at short range.

II.iii The Green's Function for the Scattered Orbits: G.

In this section we derive an expression for the Green's function $G(\underline{r},\underline{p}\,;\,\underline{r}',\underline{p}')$ defined by equations (II.i.6) and (II.ii.4). We consider the solution to the time dependent Boltzmann equation which was first

reported by Chambers (1962). We here derive the expression by using the total derivative of n_1 at any particular point. We then expect the stationary Boltzmann equation to have a similar solution and prove this to be so by substitution. We go on to discuss the reversibility of this function in the irreversible transport process, and derive the reversed Green's function explicitly.

From equation (II.i.8) the equivalent homogeneous form of the Boltzmann equation in the moving frame in the steady-state is:

$$\frac{\underline{p}}{m} \cdot \frac{\partial n_1'}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}} \cdot \frac{\partial n_1'}{\partial \underline{p}} + \frac{n_1'}{\tau} = 0 \qquad \text{(II.iii.1)}$$

The Green's function $G(\underline{r}, \underline{p}\,;\, \underline{r}', \underline{p}')$ for those orbits passing through the scattering region of V_0 satisfies the equation:

$$\frac{\underline{p}}{m} \cdot \frac{\partial G}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}} \cdot \frac{\partial G}{\partial \underline{p}} + \frac{G}{\tau} = \delta(\underline{r}-\underline{r}')\,\delta(\underline{p}-\underline{p}') \qquad \text{(II.iii.2)}$$

We look for the solution to this equation by first considering the time-dependent Boltzmann equation. The variables $\underline{r}$ and $\underline{p}$ may be written in a parametric form relative to a fixed point $(\underline{r}_0, \underline{p}_0)$:

$$\underline{r} = \underline{r}(\underline{r}_0, t) \quad ; \quad \underline{p} = \underline{p}(\underline{p}_0, t) \qquad \text{(II.iii.3)}$$

The time dependent Boltzmann equation from (II.i.6) is:

$$\frac{\partial n}{\partial t} + \frac{\underline{p}}{m} \cdot \frac{\partial n}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}} \cdot \frac{\partial n}{\partial \underline{p}} + \frac{n}{\tau} = S(\underline{r}_0, \underline{p}_0, t)$$

The total, or substantive derivative of n is:

$$\frac{Dn}{Dt} = \left.\frac{\partial n}{\partial t}\right)_{r_0 p_0} = \left.\frac{\partial n}{\partial t}\right)_{rp} + \frac{\underline{p}}{m} \cdot \frac{\partial n}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}} \cdot \frac{\partial n}{\partial \underline{p}} \qquad \text{(II.iii.4)}$$

which transforms the Boltzmann equation into:

$$\frac{Dn}{Dt} + \frac{n}{\tau} = S(t)$$

with solution:

$$n(t) = \int_0^\infty dt' \exp\left(-\frac{t'}{\tau}\right) S(t-t') \qquad \text{(II.iii.5)}$$

The Green's function for $n(t)$ satisfies the equation:

$$\frac{\partial G'}{\partial t} + \frac{G'}{\tau} = \delta(t-t_1)$$

and has the form:

$$G'(t,t_1) = \int_0^\infty dt' \exp\left(-\frac{t'}{\tau}\right) \delta(t-t'-t_1) \qquad \text{(II.iii.6)}$$

The result (II.iii.5) was first reported by Chambers (1962). With the parameter t the Green's function is a sum over a string of δ-functions; the decay factor arises out of the probability of an electron leaving the source at $t = o$, not colliding away from the phase point $(\underline{r}_o, \underline{p}_o)$, and so not being counted at time t.

We return to the stationary solution to n_1 in which the collisions occur along the orbit in phase space rather than at any one point. We expect the Green's function in this case to have a similar structure to the time dependent case except that the integral will be summed over a string of δ-functions in phase space along the orbit of the electron from its source. We define the orbit variables $\underline{R}(t)$ and $\underline{P}(t)$ to denote the position and momentum of an electron on any one orbit passing through the scattering region. The particular orbit is determined by the boundary conditions at the source: $\underline{R}(o) = \underline{r}'$; $\underline{P}(o) = \underline{p}'$

By analogy with the time dependent solution we write the Green's function for the stationary Boltzmann operator as:

$$G(\underline{r},\underline{p};\underline{r}',\underline{p}') = \int_0^\infty dt\ \delta(\underline{r}-\underline{R}(t))\,\delta(\underline{p}-\underline{P}(t))\,\exp\left(-\frac{t}{\tau}\right) \qquad (II.iii.7)$$

where $\underline{r}'$ and $\underline{p}'$ are the initial values of $\underline{R}$ and $\underline{P}$:

$$\underline{R}(0) = \underline{r}' \quad ; \quad \underline{P}(0) = \underline{p}' \qquad (II.iii.8)$$

We now use the equations of motion to obtain expressions for the $\underline{r}$ and $\underline{p}$ derivatives of this function to show that it satisfies the defining equation (II.iii.2) for the Green's function.

The equations of motion are:

$$\frac{\partial \underline{R}}{\partial t} = \frac{\underline{P}}{m} \quad ; \quad \frac{\partial \underline{P}}{\partial t} = -\frac{\partial V_0}{\partial \underline{R}} \qquad (II.iii.9)$$

Then:

$$\frac{\partial G}{\partial \underline{r}} = \int_0^\infty dt\ \frac{\partial}{\partial \underline{r}}\,\delta(\underline{r}-\underline{R}(t))\,\delta(\underline{p}-\underline{P}(t))\,\exp\left(-\frac{t}{\tau}\right) \qquad (II.iii.10)$$

We prove the identity: $\frac{\partial}{\partial t}\delta(\underline{r}-\underline{R}(t)) = -\frac{\underline{P}}{m}\frac{\partial}{\partial \underline{r}}\delta(\underline{r}-\underline{R})$ (II.iii.11)

$$\frac{\partial}{\partial t}\delta(\underline{r}-\underline{R}) = \frac{\partial \underline{R}}{\partial t}\frac{\partial}{\partial \underline{R}}\delta(\underline{r}-\underline{R}) = \frac{\underline{P}}{m}\frac{\partial}{\partial \underline{R}}\delta(\underline{r}-\underline{R}) \qquad \text{: Equations of Motion}$$

$$= \frac{\underline{P}}{m}\frac{\partial}{\partial(\underline{r}-\underline{R})}\delta(\underline{r}-\underline{R})\cdot\frac{\partial}{\partial \underline{R}}(\underline{r}-\underline{R}) \qquad \text{: Function of a Function}$$

$$= -\frac{\underline{P}}{m}\frac{\partial}{\partial \underline{r}}(\underline{r}-\underline{R})\,\delta'(\underline{r}-\underline{R})$$

with $\delta'(\underline{r}-\underline{R})$ denoting the derivative of the δ-function with respect to its argument.

$$\frac{\partial}{\partial t}\delta(\underline{r}-\underline{R}) = -\frac{\underline{P}}{m}\cdot\frac{\partial}{\partial \underline{r}}\delta(\underline{r}-\underline{R}) \qquad \text{Q.E.D.}$$

We use the identity $\underline{P}\,\delta(\underline{p}-\underline{P}) = \underline{p}\,\delta(\underline{p}-\underline{P})$ to give:

$$\frac{\underline{p}}{m}\cdot\frac{\partial G}{\partial \underline{r}} = -\int_0^\infty \left[\frac{\partial}{\partial t}\delta(\underline{r}-\underline{R}(t))\right]\delta(\underline{p}-\underline{P})\exp\left(-\frac{t}{\tau}\right)dt \qquad (\text{II.iii.12})$$

Similarly:

$$\frac{\partial G}{\partial \underline{p}} = \int_0^\infty dt\;\delta(\underline{r}-\underline{R})\frac{\partial}{\partial \underline{p}}\delta(\underline{p}-\underline{P})\exp\left(-\frac{t}{\tau}\right)$$

By an argument similar to that used to prove (II.iii.11), we may show:

$$\frac{\partial}{\partial t}\delta(\underline{p}-\underline{P}) = \frac{\partial V_0}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{p}}\delta(\underline{p}-\underline{P})$$

and then:

$$\frac{\partial V_0}{\partial \underline{r}}\cdot\frac{\partial G}{\partial \underline{p}} = \int_0^\infty dt\;\delta(\underline{r}-\underline{\rho})\left[\frac{\partial}{\partial t}\delta(\underline{p}-\underline{P})\right]\exp\left(-\frac{t}{\tau}\right) \qquad (\text{II.iii.13})$$

If we also note that:

$$\frac{G}{\tau} = \frac{1}{\tau}\int_0^\infty dt\;\delta(\underline{r}-\underline{R})\,\delta(\underline{p}-\underline{P})\exp\left(-\frac{t}{\tau}\right)$$

$$= -\int_0^\infty dt\;\delta(\underline{r}-\underline{R})\,\delta(\underline{p}-\underline{P})\left[\frac{\partial}{\partial t}\exp\left(-\frac{t}{\tau}\right)\right] \qquad (\text{II.iii.14})$$

and add equations (II.iii.12/13/14), we obtain:

$$\frac{\underline{p}}{m}\cdot\frac{\partial G}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}}\cdot\frac{\partial G}{\partial \underline{p}} + \frac{G}{\tau}$$

$$= -\int_0^\infty dt \left\{ \left[\frac{\partial}{\partial t}\delta(\underline{r}-\underline{R})\right]\delta(\underline{p}-\underline{P})\exp\left(-\frac{t}{\tau}\right) \right.$$

$$\left. + \delta(\underline{r}-\underline{R})\left[\frac{\partial}{\partial t}\delta(\underline{p}-\underline{P})\right]\exp\left(-\frac{t}{\tau}\right) + \delta(\underline{r}-\underline{R})\delta(\underline{p}-\underline{P})\left[\frac{\partial}{\partial t}\exp\left(-\frac{t}{\tau}\right)\right]\right\}$$

The terms in parentheses form an exact differential:

$$\frac{\partial}{\partial t}\left[\delta(\underline{r}-\underline{R})\delta(\underline{p}-\underline{P})\, e^{-t/\tau}\right]$$

Integrating with boundary conditions at infinity and at $t=0$

$$\frac{\underline{p}}{m}\cdot\frac{\partial G}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}}\cdot\frac{\partial G}{\partial \underline{p}} + \frac{G}{\tau} = \delta(\underline{r}-\underline{r}')\,\delta(\underline{p}-\underline{p}')$$

Since this is the defining relation for the Green's function (equation II.iii.2), we have shown that the Green's function for the stationary Boltzmann operator for any orbit is given by:

$$\boxed{G(\underline{r},\underline{p};\underline{r}',\underline{p}') = \int_0^\infty dt\, \exp\left(-\frac{t}{\tau}\right)\delta(\underline{r}-\underline{R}(t))\,\delta(\underline{p}-\underline{P}(t))}$$

with boundary conditions: $\underline{R}(0) = \underline{r}'$ (II.iii.15)

$$\underline{P}(0) = \underline{p}'$$

In this classical treatment the orbits of the scattered electrons are reversible in that electron A travelling in the opposite direction with the same speed at each point as electron B will traverse the same orbit as electron B. But the transport process as a whole is not reversible because electrons are lost from the orbit by

scattering. Electrons scattered on to the orbit are considered as a term in the homogeneous part of our equations, as a source of "new" electrons. If we consider a single electron starting out from the point $(\underline{r}', \underline{p}')$ and following an orbit which passes through the point $(\underline{r}, \underline{p})$ then the Green's function is a measure of the probability that it will reach the second point. Now this function is not reversible in the sense of changing the sign of the time variable t for then the scattering process would appear to increase the electron density. Nor does this function show any reciprocal property between $G(\underline{r}, \underline{p}; \underline{r}', \underline{p}')$ and $G(\underline{r}', \underline{p}'; \underline{r}, \underline{p})$. The equations of motion will determine the orbit momentum to within a constant which is fixed by the boundary condition at $\underline{p}'$ where the electron starts; the electron will arrive at the point $(\underline{r}, \underline{p})$ at a later time and subsequently never return to $(\underline{r}', \underline{p}')$ The Green's function $G(\underline{r}', \underline{p}'; \underline{r}, \underline{p})$ is always zero.

There is one important sense in which the Green's function is reversible and this is used later to evaluate some integrals.

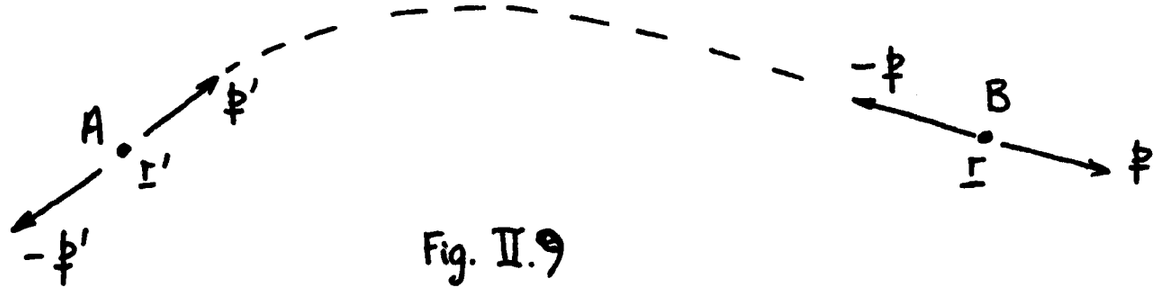


Fig. II.9

If an electron A starts out from the point $\underline{r}'$ with momentum $\underline{p}'$ then $G(\underline{r}, \underline{p}; \underline{r}', \underline{p}')$ is the probability of arriving at the point $\underline{r}$ with momentum $\underline{p}$. Now consider electron B which sets out from the point $\underline{r}$ with momentum $-\underline{p}$.

The equations of motion will determine that it will pass through the point $\underline{r}$ with momentum $-\underline{p}$ having travelled along the same orbit as A but in the opposite direction. The arrival probability is $G(\underline{r}', -\underline{p}' ; \underline{r}, -\underline{p})$. It is clear that not only are the orbits identical, but the scattering process is in the same sense, and these two Green's Functions will be the same.

$$G(\underline{r}, \underline{p} ; \underline{r}', \underline{p}') = G(\underline{r}', -\underline{p}' ; \underline{r}, -\underline{p}) \qquad (II.iii.16)$$

Mathematically this arises because both Green's functions are eigenfunctions of the Boltzmann operator, on the one hand in $(\underline{r}, \underline{p})$ space and on the other in $(\underline{r}', \underline{p}')$ space.

The reversed Green's Function is then given by:

$$G(\underline{r}', -\underline{p}' ; \underline{r}, -\underline{p}) = \int_0^\infty dt \, \exp(-\tfrac{t}{\tau}) \, \delta(\underline{r}' - \underline{R}(t)) \, \delta(\underline{p}' - \underline{P}(t))$$

with boundary conditions $R(0) = \underline{r}$; $P(0) = -\underline{p}$
In this expression t is running in the opposite sense from before. We transform this variable by $t \to -t$ in the integral noting that $R(-t) \to R(t)$ and $P(-t) \to -P(t)$

$$G(\underline{r}', -\underline{p}' ; \underline{r}, -\underline{p}) = \int_0^\infty -dt \, \exp(\tfrac{t}{\tau}) \, \delta(\underline{r}' - \underline{R}(t)) \, \delta(-\underline{p}' - \underline{P}(t))$$

with boundary conditions $\underline{R}(0) = \underline{r}$; $\underline{P}(0) = \underline{p}$
Using the identity $\delta(-x) = -\delta(x)$ we have, for the reversed Green's Function:

$$G(\underline{r}', -\underline{p}' ; \underline{r}, \underline{p}) = \int_0^{-\infty} dt \, \exp(\tfrac{t}{\tau}) \, \delta(\underline{r}' - \underline{R}(t)) \, \delta(\underline{p}' - \underline{P}(t)) \qquad (II.iii.17)$$

II.iv The Momentum Integrated Green's Function: $H(\underline{r}', \underline{r})$

We shall find in sections II.vii and II.viii in which we derive expressions for the contributions $\bar{f}_2$ and $\bar{f}_3$ that for scattered orbits we are able to write the mean distribution function of equations (II.i.7) and (II.ii.5) in the form:

$$\bar{f}(\underline{r}, \underline{p}) = \iint d^3\underline{r}' d^3\underline{p}' \, G(\underline{r}, \underline{p}; \underline{r}', \underline{p}') \, S(\underline{r}') \frac{1}{4\pi} d\omega_p \qquad (\text{II.iv.1})$$

We shall be able to write the source as a function of $\underline{r}'$ only. $\bar{n}$ is then related to $\bar{f}$ by equation (II.i.10). We use the abbreviated notation $\bar{f}(\underline{r}) = \bar{f}(\underline{r}, p)$ since the momentum is everywhere equal in magnitude to the Fermi momentum. We may now define a function $H(\underline{r}, \underline{r}')$ such that:

$$\bar{f}(\underline{r}) = \int d^3\underline{r}' \, H(\underline{r}, \underline{r}') \, S(\underline{r}') \qquad (\text{II.iv.2})$$

and

$$H(\underline{r}, \underline{r}') = \int d^3\underline{p}' \, \frac{d\omega_p}{4\pi} \, G(\underline{r}, \underline{p}; \underline{r}', \underline{p}') \Big|_{p = p_f} \qquad (\text{II.iv.3})$$

The integrals are evaluated in the region $p = p_f$ in this section. We integrate the reversed Green's function of equation (II.iii.17) with respect to $\underline{p}'$. We transform the coordinates $(p_x\, p_y\, p_z)$ to (L_1, L_2, E); we only need two components of the angular momentum because the third is determined by $\underline{L}_3 \cdot \underline{r} = 0$ as the orbit lies in a plane. We are able to carry out integrations over E and the azimuthal angle of the angular momentum Φ_L before

another transform (L, t) to (R, Θ), the orbit variables, allows us to complete the integral.

We first derive the Jacobian of the transformation into angular momentum. The phase variables (r, p) may be written in terms of two components of the angular momentum L, and the energy E. The third component of the angular momentum is superfluous because the orbit is always in a plane perpendicular to $\underline{L}$ and $r \cdot L = 0$. We consider the subset $L_x\ L_y\ E$ of the phase variables, and later generalise the solution to any orientation of the orbit. In this transformation the coordinate sub-space is invariant and we may write the inverse of the Jacobian:

$$\frac{\partial(L_x\ L_y\ E)}{\partial(p_x\ p_y\ p_z)} = \det. \begin{vmatrix} \frac{\partial L_x}{\partial p_x} & \frac{\partial L_y}{\partial p_x} & \frac{\partial E}{\partial p_x} \\ \frac{\partial L_x}{\partial p_y} & \frac{\partial L_y}{\partial p_y} & \frac{\partial E}{\partial p_y} \\ \frac{\partial L_x}{\partial p_z} & \frac{\partial L_y}{\partial p_z} & \frac{\partial E}{\partial p_z} \end{vmatrix} \qquad (\text{II. iv. 4})$$

By definition the angular momentum and energy are:

$$\begin{aligned} L_x &= y p_z - z p_y \\ L_y &= z p_x - x p_z \\ E &= \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \end{aligned} \qquad (\text{II. iv. 5})$$

The determinant is then:

$$\begin{vmatrix} 0 & z & \frac{p_x}{m} \\ -z & 0 & \frac{p_y}{m} \\ y & -x & \frac{p_z}{m} \end{vmatrix} = \frac{z}{m}\left(x p_x + y p_y + z p_z\right)$$

and

$$\frac{\partial(L_x L_y E)}{\partial(p_x p_y p_z)} = \frac{z}{m}\left(\underline{r}.\underline{p}\right)$$

We may now generalise this expression for any orientation of the orbit if we replace z by r :

$$\frac{\partial(p_x p_y p_z)}{\partial(L_1 L_2 E)} = \frac{m}{r(\underline{r}.\underline{p})}$$

The transformation we seek is:

$$d^3\underline{p} = m p \, d\omega_p \, dE = d^2\underline{L} \, dE \, \frac{\partial(p_x p_y p_z)}{\partial(L_1 L_2 E)}$$

$$\boxed{d\omega_p = \frac{d^2\underline{L}}{rp(\underline{r}.\underline{p})} = \frac{L \, dL \, d\varphi_L}{rp(\underline{r}.\underline{p})}} \qquad (II.iv.6)$$

We now return to expression (II.iv.3) and substitute the Green's function:

$$H(\underline{r},\underline{r}') = \int_0^\infty dt \, e^{-t/\tau} \int \frac{d\omega_p}{4\pi} \, \delta^3\left(\underline{r} - \underline{\rho}(t)\right) \delta^3\left(\underline{p} - \underline{P}(t)\right) d^3\underline{p}'$$

The variable of integration appears only as a boundary condition on the integrand, but we are able to use the reversibility property of equation (II.iii.16), and with the explicit form of the reversed Green's function in equation

(II.iii.17), we write:

$$H(\underline{r},\underline{r}') = \int_0^{-\infty} dt\, e^{t/\tau} \int \frac{d\omega_p}{4\pi}\, \delta^3(\underline{r}' - \underline{R}(t))\, \delta^3(\underline{p}' - \underline{P}(t))\, d^3\underline{p}'$$

The $\underline{p}'$ integration is now straightforward. We introduce the transformation (II.iv.6) into angular momentum:

$$H(\underline{r},\underline{r}') = \frac{1}{4\pi} \int_0^{-\infty} dt\, e^{t/\tau} \int \frac{L\, dL\, d\varphi_L}{rp(\underline{r}\cdot\underline{p})}\, \delta^3(\underline{r}' - \underline{R}(t)) \qquad \text{(II.iv.7)}$$

In this expression φ_L orientates the plane of the orbit.

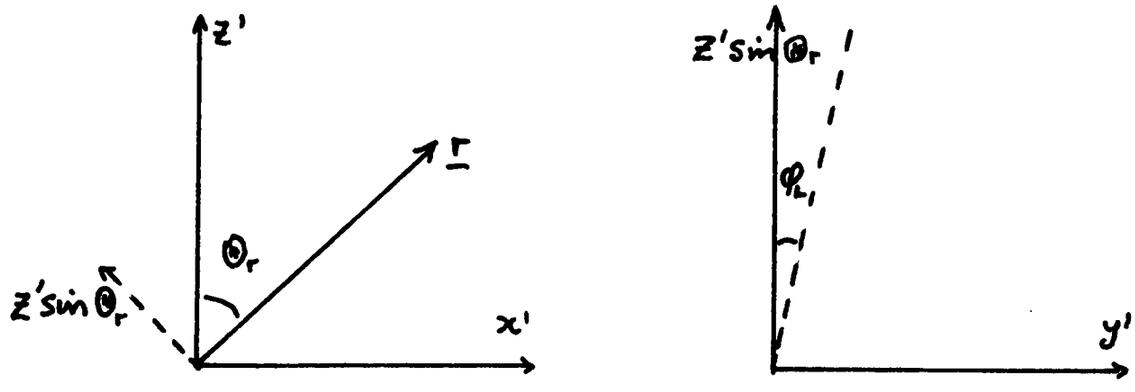


Fig. II.10

Suppose that the plane of the orbit coincides with the xz - plane of a rectangular Cartesian coordinate system. Then $L_z = 0$, and the y -coordinate of the orbit $Y(t)$ is zero for all t. We now allow a small excursion of the orbit from this plane in the form $Y(t) = \varphi_L z' \sin\Theta_r$. Θ_r is the angle between $\underline{r}$ and $\underline{r}'$, and is asymptotically equal to the compliment of the scattering angle Θ. Writing out the δ -function of equation (II.iv.7):

$$\delta^3(\underline{r}-\underline{R}) = \delta(x'-X)\, \delta(y' - z'\varphi_L \sin\Theta_r)\, \delta(z'-Z)$$

If we now reimpose the restriction that the orbit remain in the xz - plane then $y' = 0$ and:

$$H(\underline{r},\underline{r}') = \frac{1}{4\pi}\int_0^{-\infty} dt\, e^{t/\tau}\int \frac{L\,dL}{rp(\underline{r}.\underline{p})}\, d\varphi_L\, \delta(x'-x)\,\delta(y'-z'\varphi_L\sin\Theta_r)\,\delta(z'-Z)$$

Since $\int \delta(ax)\,dx = \frac{1}{a}$ we have:

$$H(\underline{r},\underline{r}') = -\frac{1}{4\pi}\int_0^{-\infty} dt\, e^{t/\tau}\int \frac{L\,dL}{rp(\underline{r}.\underline{p})}\,\frac{1}{z\sin\Theta_r}\,\delta(x'-x)\,\delta(z'-Z)$$

We may generalise this expression to any orientation of the orbit if we replace z' by r' and:

$$H(\underline{r},\underline{r}') = -\frac{1}{4\pi}\int_0^{-\infty} dt\, e^{t/\tau}\int \frac{L\,dL}{rp(\underline{r}.\underline{p})}\,\frac{1}{r'\sin\Theta_r}\,\delta^2(\underline{r}'-\underline{R}) \qquad (\text{II.iv.9})$$

where now $\delta^2(\underline{r}'-\underline{R})$ refers to the plane of the orbit.

Once more a change of variables completes the integral. Θ_r may be considered as the coordinate of the vector $\underline{R}$. L and t define an orbit of angular momentum L and parameter t on that orbit. We may transform (L,t) into (R,Θ_r) and the Jacobian of this transformation is then, with R and L as independent variables:

$$\frac{\partial(R,\Theta_r)}{\partial(L,t)} = \det\begin{vmatrix} \dot{R}\,\frac{\partial t}{\partial L} & \dot{R} \\ \frac{\partial\Theta_r}{\partial L}+\dot{\Theta}_r\frac{\partial t}{\partial L} & \dot{\Theta}_r \end{vmatrix} = \frac{\partial\Theta_r}{\partial L}\,\dot{R} \qquad (\text{II.iv.10})$$

When we make this transformation the variable t/τ in the exponential takes the form $\frac{1}{L}\int_{\underline{r}}^{\underline{R}} ds$ where

ds is an element of length on the orbit, and $l = \tau p_T/m$ is the electron mean free path. We introduce the form $(R-r)/l$ and assume that all orbits pass through the scattering centre. Since for some values of $\underline{r}$, the variable t is a double-valued function of R we divide the region of integration into (i) $r > R > 0$ for which the exponential factor is $\exp(R-r)/l$ and (ii) $0 < R < r'$ for which this factor is $\exp -(R+r)/l$.

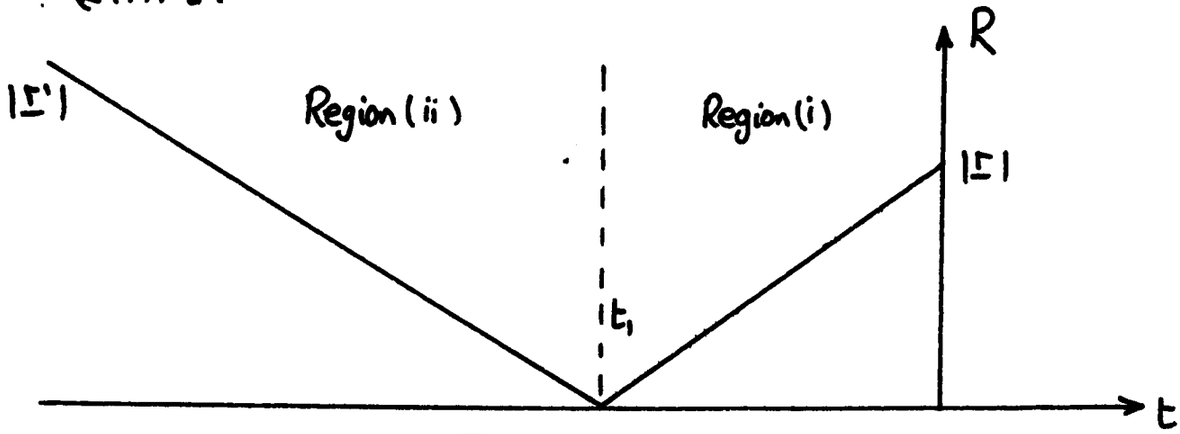


Fig II.11

We shall see in sections II.vii and II.viii that the contribution from region (i) cancels with a G_0 straight line orbit, and in region (ii) the straight-line orbit has the same radial function but the angular function is displaced by the scattering angle Θ. We only consider region (ii).

Substituting the transformation:

$$H(\underline{r},\underline{r}') = \frac{1}{4\pi}\iint \frac{d^2R}{R}\,\frac{1}{\frac{\partial\Theta}{\partial L}\dot{R}}\,\frac{L\,e^{-(R+r)/l}}{r'rp(\underline{r}.\underline{p})\sin\Theta_r}\,\delta^2(\underline{r}'-\underline{R}) \qquad (II.iv.11)$$

with $\underline{r}$ and $\underline{r}'$ on opposite sides of the ion. The integration is straightforward:

$$H(\underline{r},\underline{r}') = \frac{e^{-r/l}}{4\pi r p\,(\underline{r}\cdot\underline{p})} \quad \frac{e^{-r'/l}}{\dot{r}' r^2} \quad \frac{L}{\sin\Theta \frac{\partial\Theta}{\partial L}}$$

From the equation of motion:

$$\frac{m}{2}\left(\dot{r}^2 + \frac{L^2}{mr^2}\right) = E - V(r) = \frac{p^2}{2m}$$

from which $$m\dot{r}'r' = \sqrt{r'^2p'^2 - L^2} = (\underline{r}'\cdot\underline{p}') \qquad (\text{II}.\text{iv}.13)$$

Once more we make the approximation

$$(\underline{r}'\cdot\underline{p}') = r'p' = r'p_F$$

We note that in the expression $\bar{f}_3$ we do not have to make this approximation in the primed coordinates as we may cancel a factor $(\underline{r}'.\underline{p}')$ in the numerator.

$$H(\underline{r},\underline{r}') = \frac{m}{4\pi p_F^3} \quad \frac{e^{-r/l}}{r^2} \quad \frac{e^{-r'/l}}{r'^2} \quad \frac{L}{\sin\Theta \frac{\partial\Theta}{\partial L}}$$

The asymptotic conditions give $L = p_F b$ and

$$\frac{\partial\sigma}{\partial\omega'} = \frac{b\,db}{\sin\Theta\, d\Theta}$$

Where we have used $\Theta = \theta' - \theta$ so that $d\Theta = d\theta'$ at constant θ, and hence use of primed coordinates.

Now $$\frac{L}{\sin\Theta \frac{\partial\Theta}{\partial L}} = p_F^2 \frac{\partial\sigma}{\partial\omega'} \qquad (\text{II}.\text{iv}.14)$$

$$\boxed{H(\underline{r},\underline{r}') = \frac{m}{4\pi p_F} \quad \frac{e^{-r/l}}{r^2} \quad \frac{e^{-r'/l}}{r'^2} \quad \frac{\partial\sigma}{\partial\omega'}} \qquad (\text{II}.\text{iv}.15)$$

At this point we are able to appreciate one aspect of the problem of extending this approach to short-range. In this region we may no longer replace $(\underline{r}.\underline{p})$ by its asymptotic form $r p_F$. If L is replaced by $p_F b$ then this function varies as $p_F \sqrt{r^2 - b^2}$; the impact parameter b is a function of $(\underline{r}, \underline{p})$ See fig (II.3) The Fermi momentum p_F is also a function of r inside the region where the potential is non-zero: $p_F = \sqrt{2m(E_F - V(r))}$ The factor $(\underline{r}.\underline{p})$ will provide a cut-off in the radial part of the orbit function so that only those electrons with small impact parameters will penetrate to $r \to 0$ However, the expression relating b to $(\underline{r},\underline{p})$ is sufficiently complex to render the evaluation of the integrals fit only for extensive numerical computation.

The significant feature of the expression (II.iv.15) for H is that it factorizes. We shall take advantage of this when we want to find its Fourier transform. We now go on to derive the G_0 terms and show that they take a simple form after a Fourier transform. We shall return in the following sections to calculate the G_1 terms when we know the form of $G - G_0$.

II.v The Straight Line Orbits

We return to the straight-line orbits discussed in section II.ii. Along these orbits the electron momentum is everywhere constant. In the absence of the ionic potential V_0 the magnitude of the momentum is just $p_F = \sqrt{2m E_F}$ and its direction is parallel to the vector $\underline{r} - \underline{r}'$. We may therefore look immediately for the angular integral of the Green's function G_0 for these orbits. We integrate the defining relation (II.ii.6) and find a solution for the

integrated Green's function. We find that it takes the form $G_0(\underline{r}-\underline{r}', p_F)$ so that $G_0 S$, the contribution to the distribution function, is a convolution in coordinate space. We make a Fourier transform taking the source term by term, and evaluate the necessary transforms of $e^{-s/\ell}/s^2$ and $e^{-s/\ell}/s^3$ to write an algebraic equation for the mean distribution function in momentum space.

We factorize a term $\delta(\underline{p}-\underline{p}_0)$ with $|\underline{p}_0| = p_F$ from the Green's function and rewrite the momentum $\underline{p}$ in terms of the vector $\underline{r}-\underline{r}'$ between the test points. The momentum must be parallel to this vector. We may then write the equation for the Green's function G_0 from equation (II.ii.6):

$$\frac{p_F}{m}\frac{(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|}\cdot\frac{\partial G_0}{\partial \underline{r}} + \frac{G_0}{\tau} = \delta(\underline{r}-\underline{r}')\delta(\underline{p}-\underline{p}')$$

which has the solution:

$$\int d\omega_p\, G_0(\underline{r},\underline{p};\underline{r}',\underline{p}') = \frac{m}{p_F}\frac{e^{-|\underline{r}-\underline{r}'|/\ell}}{(\underline{r}-\underline{r}')^2}\delta(\underline{p}'-\underline{p}_0) \qquad (\text{II.v.1})$$

We see that this Green's function has the form $G_0(\underline{r}-\underline{r}', p_F)\,\delta(\underline{p}-\underline{p}_0)$. When we integrate the product $G_0 S$ over $\underline{p}'$ then we "lock-on" to the orbit whose momentum is constant, whereas when we do the same for $G_1 S$ we shall lock-on the orbits which pass through the scattering region.

The $G_0 S$ integral is now a convolution in coordinate space. The terms S_1 and S_2 are straightforward, but we shall see that S_3 can also be written in this form if we replace the momentum by $\underline{p} = p_F\frac{(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|}$

The contributions take a simple form if we make a Fourier transform into momentum k-space:

$$T\left[\int d^3\underline{r}'\, G_0(\underline{r}-\underline{r}')\, S(\underline{r}')\right] = (2\pi)^3\, \Gamma(\underline{k})\, \Sigma(\underline{k}) \qquad (\text{II.v.2})$$

with

$$\Sigma(\underline{k}) = T\left[S(\underline{r})\right] = \frac{1}{(2\pi)^3}\int d^3\underline{r}\; S(\underline{r})\, e^{-i\underline{k}\cdot\underline{r}} \qquad (\text{II.v.3})$$

and conversely: $$S(\underline{r}) = \int d^3\underline{k}\; e^{i\underline{k}\cdot\underline{r}}\; \Sigma(\underline{k})$$

The first contribution from $G_0 S_1$ with a spatially uniform source easily is seen to be zero. In coordinate space this contribution is the solution to:

$$\frac{\underline{p}}{m}\cdot\frac{\partial f_0}{\partial \underline{r}} + \frac{f_0}{\tau} = -\frac{u}{\tau}\, p_z$$

In k-space: $$\frac{i}{m}(\underline{p}\cdot\underline{k})\, g'(\underline{k}) + \frac{1}{\tau}\, g'(\underline{k}) = -\frac{u}{\tau}\, p_z\, \delta(\underline{k})$$

which has solution $g'(\underline{k}) = -u p_z\, \delta(\underline{k})$

We do not have to carry out the inverse transform to see that integration over $\underline{p}$ will give zero contribution. However the transform is straightforward and we find the result of equation (II.i.17)

$$n_1^0 = -u p_z \frac{\partial n_0}{\partial E} \qquad (\text{II.v.4})$$

which is the density arising from the transformation into the moving frame of the ion, without any electrostatic effect.

We go on to the second term $S_2 = \bar{n}_1/\tau$ which gives a contribution

$$\bar{f}_2 \frac{\partial n_0}{\partial E} = \int G_0 S_2 = \frac{1}{\tau}\int d^3\underline{r}' d^3\underline{p}'\; G_0(\underline{r}-\underline{r}')\, \nu(r')\, z' \frac{\partial n_0}{\partial E}\, \frac{d\omega_p}{4\pi}$$

We define $\bar{g}(\underline{k})$ as the Fourier transform of the mean distribution function:

$$\bar{g}(\underline{k}) = \frac{1}{8\pi^3} \int d^3\underline{r}\ e^{-i\underline{k}.\underline{r}}\ \nu(r) z \qquad (II.v.5)$$

The contribution $\int G_0 S_2$ to $\bar{g}(\underline{k})$ is then given by the algebraic product

$$\frac{1}{4\pi} G_0(\underline{k}) \frac{1}{\iota} \bar{g}(\underline{k}) = T\left[\frac{e^{-s/\iota}}{s^2}\right] \frac{(2\pi)^3}{4\pi\iota} \bar{g}(\underline{k}) \qquad (II.v.6)$$

with $\underline{s} = \underline{r} - \underline{r}'$. Before going on to consider the third contribution we evaluate the transform in (II.v.6)

$$(2\pi)^3 T\left[\frac{e^{-s/\iota}}{s^2}\right] = \int d^3\underline{s}\ e^{-i\underline{k}.\underline{s}}\ \frac{e^{-\gamma s}}{s^2} \qquad (\gamma = \tfrac{1}{\iota})$$

$$= 2\pi \int ds\ d(\cos\theta)\ e^{-\gamma s}\ e^{-iks\cos\theta}$$

$$= \frac{2\pi}{ik} \int ds\ \frac{e^{-\gamma s}}{s} \left(e^{iks} - e^{-iks}\right) = \frac{4\pi}{k} \int_0^\infty ds\ \frac{e^{-\gamma s}}{s} \sin ks$$

The Fourier sine transform of $e^{-\gamma s}/s$ is $\tan^{-1} k/\gamma$ or $\tan^{-1} k\iota$ from (Ref: Bateman Project 1954) and the transform we seek is:

$$T\left[\frac{e^{-s/\iota}}{s^2}\right] = \frac{1}{2\pi^2 k} \tan^{-1} k\iota \qquad (II.v.7)$$

The contribution from $G_0 S_2$ is $\boxed{\frac{1}{k\iota} \tan^{-1} k\iota\ \bar{g}(\underline{k})}$ (II.v.8)

In the third source term we have a $\hat{p}'$ dependence, and the transform is not so straightforward. In coordinate space:

$$\frac{1}{4\pi}\int G_0 S_3 \, d^3\underline{r}' \, d^3\hat{p}' \, d\omega_{\hat{p}} = \frac{1}{4\pi}\iint d^3\underline{r}' \, d^3\hat{p}' \; \frac{e^{-|\underline{r}-\underline{r}'|/\ell}}{(\underline{r}-\underline{r}')^2} \; \delta(\hat{p}'-\hat{p}_0) \; \underset{p'}{\underline{\hat{p}}'} \cdot \frac{\partial V_1}{\partial \underline{r}'} \qquad (\text{II.v.9})$$

We make use of the relation between the direction of $\hat{p}'$ and that of the vector $\underline{r}-\underline{r}'$ to write:

$$\frac{\underline{p}'}{p'} = \frac{(\underline{r}-\underline{r}')}{|\underline{r}-\underline{r}'|} = \frac{\underline{S}}{S} \qquad \text{with} \quad \underline{S} = \underline{r}-\underline{r}' \qquad (\text{II.v.10})$$

In this notation the contribution from S_3 is:

$$\frac{1}{4\pi}\int d^3\underline{r}' \; \frac{e^{-S/\ell}}{S^3} \; \underline{S} \cdot \frac{\partial}{\partial \underline{r}'} V_1(\underline{r}')$$

Once more the convolution is transformed to a simple product in momentum space:

$$-\frac{i}{4\pi}\left\{ \frac{\partial}{\partial \underline{k}} \int d^3\underline{S} \; e^{i\underline{k}\cdot\underline{S}} \; \frac{e^{-S/\ell}}{S^3} \right\} \cdot T\left\{ \frac{\partial}{\partial \underline{r}'} \int d^3\underline{k} \; V_1(\underline{k}) \, e^{-i\underline{k}\cdot\underline{r}} \; \frac{1}{4\pi} \right\}$$

$$= -i\,\frac{(2\pi)^3}{4\pi}\,\frac{\partial}{\partial \underline{k}}\, T\left[\frac{e^{-S/\ell}}{S^3}\right] \cdot (-i\underline{k})\, T\left[V_1(\underline{r}')\right]$$

$$= -(2\pi)^3 \,\frac{\partial}{\partial k}\, T\left[\frac{e^{-S/\ell}}{S^3}\right] \,\frac{k}{4\pi}\, T\left[V_1(\underline{r}')\right] \qquad (\text{II.v.11})$$

The scalar product has been simple here because both transforms are spherically symmetric functions of $\underline{k}$. From the Poisson equation:

$$\nabla^2 V_1 = + \alpha^2 \nu(r) z$$

or

$$k^2 T[V_1] = - \alpha^2 \bar{g}(\underline{k}) \qquad (II.v.12)$$

The other transform in (II.v.11) may be reduced to terms involving the same Fourier sine transform of (II.v.7).

$$(2\pi)^3 T\left[\frac{e^{-s/l}}{s^3}\right] = \frac{2\pi}{ik}\int_0^\infty ds \; \frac{e^{-\gamma s}}{s^2}\left(e^{iks} - e^{-iks}\right) \qquad (II.v.13)$$

Integrating by parts:

$$= \frac{4\pi}{k}\left[-\frac{e^{-\gamma s}}{s}\sin ks\right]_0^\infty + \frac{2\pi}{ik}\int_0^\infty \frac{ds}{s}\left\{-(\gamma-ik)e^{-(\gamma-ik)s} + (\gamma+ik)e^{-(\gamma+ik)s}\right\}$$

Separating the terms in brackets:

$$= 4\pi - \frac{2\pi\gamma}{ik}\int_0^\infty \frac{ds}{s} e^{-\gamma s}\left(e^{iks} - e^{-iks}\right) + \int_0^\infty 2\pi \frac{ds}{s}\left(e^{-(\gamma-ik)s} + e^{-(\gamma+ik)s}\right)$$

$$= 4\pi - \frac{4\pi}{kl}\tan^{-1} kl + \int_0^\infty 2\pi \frac{ds}{s}\left(e^{-(\gamma-ik)s} + e^{-(\gamma+ik)s}\right)$$

where we have used the result of (II.v.7) in the second term. We are looking for the k derivative:

$$\frac{\partial}{\partial k} T\left[\frac{e^{-s/l}}{s^3}\right] = \frac{4\pi}{k^2 l} \tan^{-1} kl - \frac{4\pi}{kl} \frac{\partial}{\partial k} \tan^{-1} kl + 2\pi i \int_0^\infty ds \left(e^{-(\gamma - ik)s} - e^{-(\gamma + ik)s} \right)$$

Using $\frac{\partial}{\partial k} \tan^{-1} kl = \frac{l}{1 + k^2 l^2}$, and:

$$\int_0^\infty ds \left\{ e^{-(\gamma - ik)s} - e^{-(\gamma + ik)s} \right\} = - \left[\frac{e^{-(\gamma - ik)s}}{\gamma - ik} + \frac{e^{-(\gamma + ik)s}}{\gamma + ik} \right]_0^\infty = \frac{2ik}{\gamma^2 + k^2}$$

to give:

$$(2\pi)^3 \frac{\partial}{\partial k} T\left[\frac{e^{-s/l}}{s^3}\right] = \frac{4\pi}{k^2 l} \tan^{-1} kl - \frac{4\pi}{k(1 + k^2 l^2)} - \frac{4\pi kl^2}{1 + k^2 l^2}$$

$$\boxed{\frac{\partial}{\partial k} T\left[\frac{e^{-s/l}}{s^3}\right] = \frac{1}{2\pi^2 k} \left(\frac{\tan^{-1} kl}{kl} - 1 \right)} \qquad (\text{II.v.14})$$

From (II.v.11, 12, 14) we obtain the contribution to $G_0 S_3$:

$$\frac{\alpha^2}{k^2} \left(\frac{\tan^{-1} kl}{kl} - 1 \right) \bar{g}(\underline{k}) \qquad (\text{II.v.15})$$

With the result (II.v.8) we obtain the total contribution to $\bar{g}$ which is due to the straight-line orbits. We write this as $\bar{g}_0$:

$$\boxed{\bar{g}_0 = \bar{g} \left\{ \frac{\tan^{-1} kl}{kl} + \frac{\alpha^2}{k^2} \left(\frac{\tan^{-1} kl}{kl} - 1 \right) \right\}} \qquad (\text{II.v.16})$$

This is the exact contribution for all possible and impossible straight line orbits. We subtract the "impossible" orbits originating in the shadow of the ion in the following sections. In sections vi, vii, and viii

we calculate the contributions to $\bar{g}_1$ from the three source terms for those orbits passing through the scattering region. We return to expression (II.v.16) in section ix. when we have completed the equation for $\bar{g} = \bar{g}_0 + \bar{g}_1$.

II.vi The Scattered Orbits with spatially uniform source S_1.

We derive an expression for the integrated product $G_1 S_1$ for all orbits. We have found in section v. that the straight line orbits give no contribution $G_0 S_1$ from the spatially uniform source. This contribution f_1 is then:

$$f_1 = G S_1 \qquad \text{(II.vi.1)}$$

with

$$S_1 = -\frac{u}{\tau} p_z \frac{\partial n_0}{\partial E}$$

We use the reversibility of the Green's function and introduce the equation to the orbit on our model in which all orbits are straight lines into and out of the scattering region. We obtain the same term due to the change of frame into that of the moving ion as we have already found (II.v.4). We finally evaluate the average $\bar{f}_1$ by introducing the impact parameter of the orbits; the integral may then be expressed in terms of the transport cross-section Q.

The reversibility of the Green's function expressed in (II.iii.16)

$$G(\underline{r}, \underline{p}; \underline{r}', \underline{p}') = G(\underline{r}', -\underline{p}'; \underline{r}, -\underline{p})$$

enables us to write the product $G S_1$ with the variables of integration appearing explicitly in the integrand.

$$f_1(\underline{r}, \underline{p}) = -\frac{u}{\tau} \int_0^{-\infty} dt\, e^{t/\tau} \int \delta^3(\underline{r}' - \underline{R})\, d^3\underline{r}' \int \delta^3(\underline{p}' - \underline{P})\, p_z'\, d^3\underline{p}' \qquad \text{(II.vi.2)}$$

with boundary conditions $\underline{R}(0) = \underline{r}$; $\underline{P}(0) = \underline{p}$. The integrations are straightforward and we define $\Theta(t)$ as the instantaneous orientation of the momentum to the z-axis.

$$f_1(\underline{r},\underline{p}) = -\frac{u p_F}{\tau}\int_0^{-\infty} dt\ e^{t/\tau}\cos\Theta(t) \qquad \text{(II.vi.3)}$$

We use the approximation to the orbit that outside the scattering region the momenta have their asymptotic values as shown in figure II.3a. If the scattering region is small compared with the mean free path of the electrons then $\Theta(t)$ may be considered as a step-function as in figure II.12:

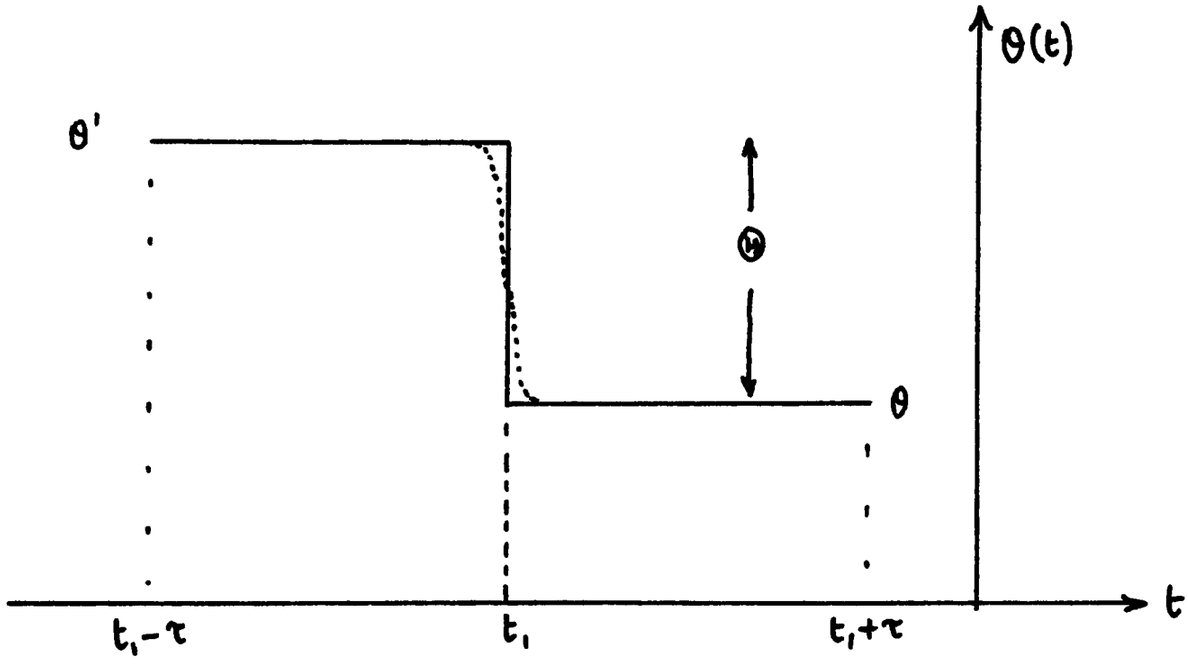


Fig II.12

Since the orbit is unique Θ' is a function of the variables $\underline{r}$ and $\underline{p}$ and is related to Θ by the scattering angle θ :

$$\Theta' = \Theta + \theta$$

The integral (II.v.3) may be divided about the "impact time" t_1 .

$$f_1(r,p) = -\frac{u}{\tau} p_F \left\{ \int_0^{t_1} dt \cos\theta\, e^{t/\tau} + \int_{t_1}^{-\infty} dt\, e^{t/\tau} \cos\theta' \right\}$$

and since $t_1/\tau = -r/l$:

$$f_1(r,p) = -u p_F \left\{ \cos\theta + e^{-r/l}(\cos\theta' - \cos\theta) \right\} \qquad \text{(II.vi.3)}$$

In terms of momentum p:

$$f_1(r,p) = -u p_z - u\, e^{-r/l} (p_z' - p_z) \qquad \text{(II.vi.4)}$$

We note here that the function Φ defined in section II.i is given by:

$$\Phi(r,p) = n_1 + u p_z \frac{\partial n_0}{\partial E} = (f + u p_z) \frac{\partial n_0}{\partial E}$$

We recall the result of section II.v that the contribution to the distribution function from the spatially uniform source along the unscattered orbit (II.v.4):

$$n_1^0 = -u p_z \frac{\partial n_0}{\partial E}$$

and we can see that there is no contribution to Φ before scattering, for the straight line orbits $(p_z' = p_z)$ which will later be scattered. In sections II.vii and II.viii we shall show that f_2 and f_3 have no contribution from upstream of the scattering centre and $\Phi = 0$ in this region. This is a consequence of the ignorance of the electrons in this region of their impending collision; they are completely unaware and unaffected by the scattering until they enter the small region near the ion.

We subtract the $G_0 S_1$ term of equation (II.v.4) (which vanishes on integration) to give $G_1 S_1$ as:

$$\int G_1 S_1 \quad = \quad -u\, e^{-r/l}\,(p_z' - p_z) \qquad \text{(II.vi.5)}$$

We shall find for sources S_2 and S_3 that we are only able to calculate the average values of these contributions, and at long range. We introduce the impact parameter b:

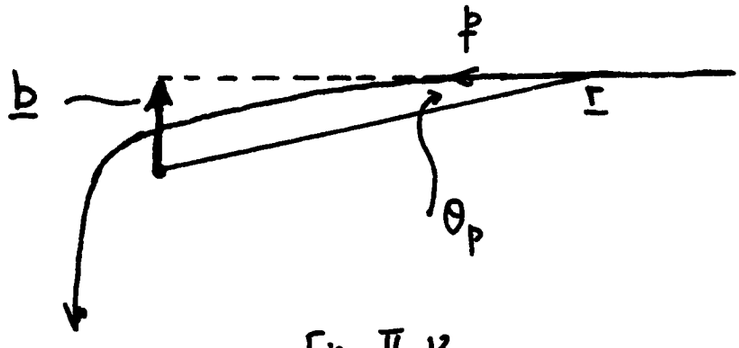


Fig. II.13

The impact parameter is the perpendicular distance from the ionic origin to the asymptotic momentum p. Then if θ_p is the angle between the position vector r and p, as in Figure II.13 and 3:

$$b = r \sin\theta_p$$

$$(r.p) = rp\cos\theta_p$$

and

$$d\omega_p = \sin\theta_p\, d\theta_p \quad = \quad \frac{b\,db}{r^2\cos\theta_p} \qquad \text{(II.vi.6)}$$

The average is then given by:

$$\bar{f}_1 = \frac{1}{4\pi}\int f_1\, d\omega_p \quad = \quad -\frac{u}{4\pi}\, e^{-r/l} \int (p_z' - p_z)\, \frac{b\,db}{r(r.p)} \qquad \text{(II.vi.7)}$$

On integration with respect to ω_p the terms perpendicular

to $\underline{r}$ vanish and we need only consider the z component of the term parallel to $\underline{r}$. Using the identity:

$$\underline{p} = \frac{\underline{p}\cdot\underline{r}}{r^2}\,\underline{r} - \frac{1}{r^2}(\underline{r}\wedge\underline{L})$$

$$p_z = \frac{\underline{p}\cdot\underline{r}}{r^2}\,z + \text{terms perpendicular to } \underline{r} \qquad (\text{II.vi.8})$$

In expression (II.vi.7):

$$\bar{f}_1 = -\frac{up_F}{4\pi}\,e^{-r/l}\int b\,db\,\cos\theta\,(\cos\Theta - 1)\,\frac{1}{r(\underline{r}\cdot\underline{p})}\cdot\frac{(\underline{r}\cdot\underline{p})}{r}$$

$$= \frac{up_F}{4\pi}\,\frac{z}{r^3}\,e^{-r/l}\int b\,db\,(1-\cos\Theta)$$

The transport cross-section is given by:

$$Q = \int b\,db\,(1-\cos\Theta)$$

so

$$\boxed{\bar{f}_1(\underline{r},\underline{p}) = up_F Q\,\frac{e^{-r/l}}{4\pi r^2}\,\frac{z}{r}} \qquad (\text{II.vi.9})$$

The expression (II.vi.9) is the contribution from the spatially uniform source summed over the family of scattered orbits. In using an impact parameter even inside the scattering region we have made approximations which have

resulted in a z / r^3 singularity at the origin. We do, however, expect this result to describe the electron density outside the scattering region.

II.vii The Scattered Orbits with the Mean Distribution Source S_2 .

We consider the second term in the source from equation (II.ii.2). We calculate the contribution from the scattered orbits $G S_2$ which we denote $\bar{f}_2'$ and subtract the contribution from the straight orbits $G_0 S_2$ denoted $\bar{f}_2''$. The difference is $\bar{f}_2$:

$$\bar{f}_2(r) = \bar{f}_2' - \bar{f}_2'' = \frac{1}{\tau} \int_{\substack{\text{Orbits} \\ \text{thro' ion}}} (G - G_0) \bar{f}(\underline{r}') d^3\underline{r}' d^3\underline{p}' d\omega_p \qquad (II.vii.1)$$

We use the result of section II.iv for the momentum integrated Green's function to evaluate $G\bar{f}$. It is due to the difficulty in calculating the complete distribution function f_2 that we only derive an expression for $\bar{f}_2$ here. The main advantage, the factorization of the mean contribution, considerably simplifies later calculation when we wish to take a Fourier transform. We use the expression for G_0 obtained in section II.v to evaluate $G_0\bar{f}$ and when subtracted from $G_1\bar{f}$ the radial factors are identical and angular factors lead to the transport cross-section.

We cancel the factor $\partial n_0 / \partial E$ and the contribution $\bar{f}_2'(r)$ from the scattered orbits is:

$$\bar{f}_2'(\underline{r}) = \frac{1}{\tau} \int G(\underline{r}, \underline{p}; \underline{r}', \underline{p}') \bar{f}(\underline{r}') d^3\underline{r}' d^3\underline{p}' d\omega_p \qquad (II.vii.2)$$

In equation (II.i.11) we wrote the mean distribution function

in the form $\bar{f}(\underline{r}') = \nu(r')\, z'$ and since the source is then a function of $\underline{r}'$ only we may use equation (II.iv.15) for the momentum integrated Green's function $H(\underline{r},\underline{r}')$:

$$\bar{f}_2'(\underline{r}) = \frac{1}{\tau}\int H(\underline{r},\underline{r}')\,\nu(r')\,z'\,d^3\underline{r}'$$

$$= \frac{m}{\tau p_F}\,\frac{e^{-r/l}}{4\pi r^2}\int_0^\infty \frac{e^{-r'/l}}{r'^2}\,\frac{\partial\sigma}{\partial\omega'}\,\nu(r')\,z'\,d^3\underline{r}' \qquad \text{(II.vii.3)}$$

We must now subract the contributions from the straight line orbits that lie in the shadow of the scattering region and which have been added to the G_0 expression in section II.iv. We discussed in section II.ii how we could take the orbits in pairs for any particular impact parameter. The contribution through G_0 , $\bar{f}_2''$, is related to a source $\bar{f}$ at some z_2' ($r_2' = r'$) in the shadow as shown in figure II.14a:

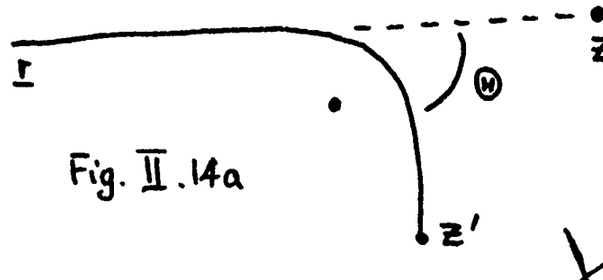


Fig. II.14a

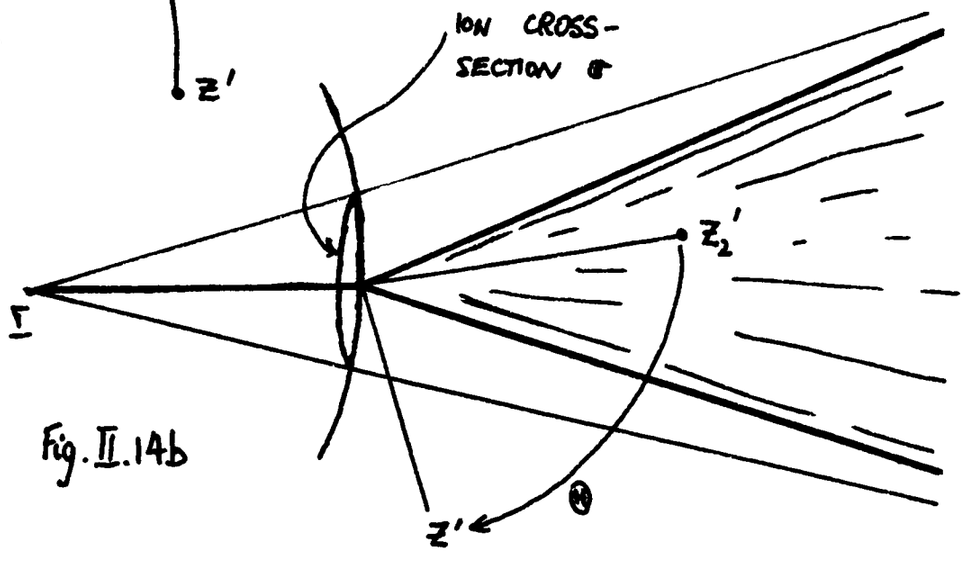


Fig. II.14b

We are able to use the function $H(r, r')$ again with a source at z' as shown in figure II.14b. We may use the more general Green's function for scattered orbits in this case for the straight orbit will have zero deflection $(\Theta = 0)$. Then $z_2'/r' = z/r$ and we have:

$$\bar{f}_2'' = \frac{m}{\tau \rho_F} \frac{e^{-r/l}}{4\pi r^2} \int_0^\infty \frac{e^{-r'/l}}{r'} \frac{\partial \sigma}{\partial \omega'} \nu(r') \frac{z}{r} d^3\underline{r}' \qquad (II.vii.4)$$

We note that this result may also be obtained using the geometry of figure II.14b and the result for $\bar{G}_0$ of equation (II.v.1). The factor $\frac{1}{4\pi r^2} \frac{\partial \sigma}{\partial \omega'} d\omega'$ is the fraction of the orbits from $d\omega'$, passing through $\underline{r}$; the exponential factor represents the scattering out. The factor $\frac{m}{\rho_F} \frac{e^{-r/l}}{r^2}$ is the Green's function $\int d\omega_p \, G_0(0, p; \underline{r}', p')$ from $\underline{r}'$ to the ion. Using $\frac{m}{\tau \rho_F} = \frac{1}{l}$ we subtract (II.vii.(3-4)) to give:

$$\bar{f}_2 = \frac{1}{l} \frac{e^{-r/l}}{4\pi r^2} \int_0^\infty dr' \, e^{-r'/l} \, r' \nu(r') \int \frac{\partial \sigma}{\partial \omega} (\cos\Theta' - \cos\Theta) d\omega' \qquad (II.vii.5)$$

In the last factor $\Theta' = \Theta + \Phi$ and integration over the polar angle will result in zero contribution for the terms in $\sin\Theta$ and this factor is just:

$$\cos\Theta \int \frac{\partial \sigma}{\partial \omega'} (\cos\Phi - 1) d\omega' = -\cos\Theta \, Q$$

with the transport cross-section, Q. Finally:

$$\boxed{\bar{f}_2(\underline{r}) = -\frac{Q}{l} \frac{e^{-r/l}}{4\pi r^2} \frac{z}{r} \int_0^\infty dr' \, e^{-r'/l} \, r' \nu(r')} \qquad (II.vii.6)$$

We shall return to this result in the final section, but we can already see that it contains the same radial dependence as the $\bar{f}_1$ of section II.vi. In this case the singularity in r is related to the approximation $(\underline{r}.\underline{p}) = rp$ for the exact function will provide a cut-off at a minimum radius where $(\underline{r}.\underline{p}) = 0$ The function $(\underline{r}.\underline{p})^{-1}$ is an integrable function since it varies as $1/x$ near $x = 0$. A more detailed analysis to include the structure of the orbit would not be expected to give a singularity of such high order. Our approximation has taken all orbits to pass through the ionic origin and this is only their apparent behaviour in the asymptotic region. In practise angular momentum conservation will prevent any electrons from penetrating to the ionic origin.

II.viii The Scattered Orbits with the Electrostatic Source S_3.

We consider the final term in the source (equation II.ii.2)

$$\frac{\partial V_1}{\partial \underline{r}} \cdot \frac{\underline{p}}{p} \frac{\partial n_0}{\partial p} = \frac{p_F}{m} \left(\frac{\partial V_1}{\partial \underline{r}} \cdot \frac{\underline{p}}{p} \right) \frac{\partial n_0}{\partial \varepsilon}$$

In this case the source contains two terms related firstly to z , and secondly to p_z . We consider their contributions to $\bar{f}_3 = \overline{G_1 S_3}$ separately. We consider the contribution $\bar{f}'_{3z}$ from the scattered orbits and the z source and subtract $\bar{f}''_{3z}$ from the straight line orbits with the same source. This calculation is similar to that for $\bar{f}_2$ in the previous section. The source term S_{3p_z} contributes to $\bar{f}_{3p_z} = \overline{G S_{3p_z}}$ and this is calculated in a similar manner to f_1 . In this case we again make the approximation that $(\underline{r}.\underline{p}) = rp$

everywhere. In both these calculations we use the result of equations (II.i.12,13) to relate the function μ in the potential to the function $\nu(r)$ in the electron density.

Factorizing a term in $\partial n_0/\partial E$ we have for the scattered orbits:

$$f_3(\underline{r},\underline{p}) = \frac{p_F}{m}\iint G_1(\underline{r},\underline{p};\underline{r}',\underline{p}')\frac{1}{p'}\left(\underline{p}'\cdot\frac{\partial V_1}{\partial \underline{r}}\right)d^3\underline{r}'\,d^3\underline{p}' \qquad (\text{II.viii.1})$$

With $V_1 = z\mu(r)$ we may write the source term:

$$\underline{p}\cdot\nabla V_1 = \underline{p}\cdot\nabla(\mu z) = z(\underline{p}\cdot\nabla\mu) + \mu(\underline{p}\cdot\hat{\underline{z}})$$

$$= \frac{z}{r}(\underline{p}\cdot\underline{r})\frac{\partial\mu}{\partial r} + \mu p_z \qquad (\text{II.viii.2})$$

We write the contribution f_3 in two terms: $f_{3z} + f_{3p_z}$ where:

$$\left.\begin{aligned} f_{3z}(\underline{r},\underline{p}) &= \frac{p_F}{m}\iint G_1(\underline{r},\underline{p};\underline{r}',\underline{p}')\frac{(\underline{r}'\cdot\underline{p}')}{r'p'}\frac{\partial\mu}{\partial r'}z'\,d^3\underline{r}'\,d^3\underline{p}' \\ f_{3p_z}(\underline{r},\underline{p}) &= \frac{p_F}{m}\iint G_1(\underline{r},\underline{p};\underline{r}',\underline{p}')\frac{p_z'}{p'}\mu(r')\,d^3\underline{r}'\,d^3\underline{p}' \end{aligned}\right\} (\text{II.viii.3})$$

The first term is averaged over ω_p and we can use the momentum integrated Green's function of section (II.iv) $H(\underline{r},\underline{r}')$. The factor $(\underline{r}\cdot\underline{p})$ does cancel with a similar factor in the denominator of $H(\underline{r},\underline{r}')$ and this was pointed out at the time, but in any case we have elsewhere made the approximation $(\underline{r}'.\underline{p}') = r'p'$ and so the source is just $S(r') = \partial\mu/\partial r'\cdot z'$. This has an identical structure to $\nu(r')z'$ in the source S_z of the

previous section. We do not repeat the entire argument of deriving the scattered term and subtracting a similar unscattered term; it will suffice to replace $\nu(r')/\tau$ in expression (II.vii.6) by $\frac{p_F}{m}\frac{\partial\mu}{\partial r'}$:

$$\bar{f}_{3z}(\underline{r}) = -Q\,\frac{e^{-r/l}}{4\pi r^2}\,\frac{z}{r}\int_0^\infty dr'\, e^{-r'/l}\, r'\,\frac{\partial\mu}{\partial r'}$$

Using expression (II.i.17) relating $\frac{\partial\mu}{\partial r'}$ to $\nu(r)$ from the Poisson equation we obtain:

$$\boxed{f_{3z}(\underline{r}) = \alpha^2 Q\,\frac{e^{-r/l}}{4\pi r^2}\,\frac{z}{r}\int_0^\infty dr'\,\frac{e^{-r'/l}}{r'^3}\int_0^{r'} dr''\, r''^4\,\nu(r'')} \qquad (\text{II.viii.4})$$

In the second term of (II.viii.3) we introduce the reversed Green's function:

$$f_{3p_z}(\underline{r},\underline{p}) = \frac{p_F}{m}\iint d^3\underline{r}'\,d^3\underline{p}'\; G_1(\underline{r}',-\underline{p}';\underline{r},-\underline{p})\,\mu(r')\,\frac{p_z'}{p'}$$

We consider first the contribution f'_{3p_z} from the scattered orbits and substitute for the complete Green's function G from equation (II.iii.17). The $\underline{r}'$ and $\underline{p}'$ integration is straightforward:

$$f'_{3p_z}(\underline{r},\underline{p}) = \frac{p_F}{m}\int_0^{-\infty} dt\; e^{t/\tau}\,\mu(R(t))\,\frac{P_z(t)}{P(t)} \qquad (\text{II.viii.5})$$

Using the identity (II.vi.3) we replace $P_z(t)$ by $\left(\frac{\underline{R}.\underline{P}}{RP}\right)z(t)$ and integrate over the polar angle to

eliminate the terms in sin θ_{RP} .

$$\bar{f}_{3p_z}(\underline{r},\underline{p}) = \frac{p_F}{4\pi m}\int_0^{-\infty} dt\, e^{t/\tau}\,\mu(R(t))\,\frac{(\underline{R}\cdot\underline{P})}{R^2 P}\,Z(t)\,p\,\frac{b\,db}{r(\underline{r}\cdot\underline{p})} \qquad (II.viii.6)$$

We divide the region of integration about the impact instant t_1 and replace $(\underline{R}\cdot\underline{P})$ by RP in each region. Then Z/R becomes cos $\theta(t)$ where $\theta(t)$ is the step-function discussed in section II.vi and shown graphically in figure II.12.

$$\frac{Z}{R} = \begin{cases} \cos\theta' & t < t_1 \\ \cos\theta & t > t_1 \end{cases}$$

We may now subtract the G_0 terms arising in the straight line orbits for then $\theta(t) = \theta$ for all t. The contribution from $t > t_1$ vanishes and we subtract a term in cos θ from the region $t_1 < t$ to give:

$$\bar{f}_{3p_z}(\underline{r}) = \frac{1}{4\pi r^2}\int_{-|t_1|}^{-\infty} dt\,\frac{p_F}{m}\,e^{t/\tau}\,\mu(R(t))\int b\,db\,(\cos\theta - 1)\cos\theta$$

In this region we may change the variable to r' by:

$$dr' = -\frac{p_F}{m}dt \quad ; \quad \mu(R(t)) = \mu(r') \qquad (II.viii.7)$$

and

$$\frac{t}{\tau} = -\frac{r+r'}{l}$$

$$\bar{f}_{3p_z}(\underline{r}) = \frac{Q}{4\pi r^2}\,\frac{z}{r}\int_0^{\infty} dr'\, e^{-(r+r')/l}\,\mu(r')$$

and with expression (II.i.18) relating μ and ν through the Poisson equation:

$$\bar{f}_{3p_z}(\underline{r}) = -\frac{\alpha^2 Q}{3}\frac{e^{-r/l}}{4\pi r^2}\frac{z}{r}\int_0^\infty dr' e^{-r'/l}\left\{\frac{1}{r'^3}\int_0^{r'} dr'' r''^4 \nu(r'') + \int_{r'}^\infty dr'' r'' \nu(r'')\right\} \quad (\text{II.viii.8})$$

Adding the contributions (II.viii.4) and (II.viii.8) we have:

$$\boxed{\bar{f}_3(\underline{r}) = \alpha^2 Q \frac{e^{-r/l}}{4\pi r^2}\frac{z}{r}\frac{1}{3}(2B-C)}$$

$$B = \int_0^\infty dr' \frac{e^{-r'/l}}{r'^3}\int_0^{r'} dr'' r''^4 \nu(r'') \qquad (\text{II.viii.9})$$

$$C = \int_0^\infty dr' e^{-r'/l}\int_{r'}^\infty dr'' r'' \nu(r'')$$

We remember here that $\nu(r)$ is derived from the complete solution to the mean distribution function from all orbits. We now look for the solution to this function before considering the evaluation of the constants.

II.ix The Solution for $\bar{g}(\underline{k})$.

We add the terms from the scattered orbits G, S derived in sections vi, vii, and viii. We find that all three terms have the same spatial variation and it remains to calculate the constants. Then we make a Fourier Transform of this function to complete the algebraic equation for the transformed mean distribution function $\bar{g}(\underline{k})$. We note

the similarity with an equation obtained by Peierls after making the approximation of weak charge on the ion. The solution to the algebraic equation is straightforward but a simple inverse transform leads to divergent results for the force and we start to discuss a cut-off mechanism that is followed up in chapter IV.

From equations (II.vi.9), (II.vii.6), (II.viii9), we have:

$$\bar{f}_1 + \bar{f}_2 + \bar{f}_3 = Q\,\frac{e^{-r/l}}{4\pi r^2}\,\frac{z}{r}\left\{ up_F - \frac{A}{l} + \frac{\alpha^2}{3}(2B-C)\right\} \qquad \text{(II.ix.1)}$$

where $$A = \int_0^\infty dr'\, e^{-r'/l}\, \nu(r')\, r'$$

and B and C are given in (II.viii.9). We may express this contribution from the scattered orbits in terms of a dimensionless constant ξ :

$$\overline{G_1 S} = \bar{f}_1 + \bar{f}_2 + \bar{f}_3 = \xi\, up_F\, Q\,\frac{e^{-r/l}}{4\pi r^2}\,\frac{z}{r} \qquad \text{(II.ix.2)}$$

with $$\xi = 1 - \frac{A}{l\,up_F} + \frac{\alpha^2}{3up_F}(2B-C)$$

Since the constants are linear integrals of ν we may define constants A' , B' , and C' which are just numerical integrals of the dimensionless quantity $\nu/up_F\xi$. Then:

$$\xi = 1 - \xi\epsilon$$

with $$\epsilon = \frac{1}{l}\int_0^\infty dr'\, e^{-r'/l}\, r'\,\frac{\nu(r')}{up_F\xi} - \frac{\alpha^2}{3}\int_0^\infty dr'\, e^{-r'/l}\left\{\frac{2}{r'^3}\int_0^{r'} dr''\, r''^4\,\frac{\nu(r'')}{up_F\xi} - \int_{r'}^\infty dr''\, r''\,\frac{\nu(r'')}{up_F\xi}\right\} \qquad \text{(II.ix.3)}$$

Then $$\boxed{\xi = \frac{1}{1+\epsilon}} \qquad \text{(II.ix.4)}$$

Equations (II.ix. 3 and 4) are the defining relations, but we cannot do much with them until we have solved the equation for $\nu(r)$ which will involve the contribution from the straight line orbits. We are able to see, from equation II.ix.2, the advantage of writing the Green's function in a form which factorized. We transform the expression to give $\bar{g}_1(\underline{k})$ the contribution to $\bar{g}(\underline{k})$ from these scattered orbits. Using the result (II.v.14) for the Fourier transform:

$$\bar{g}_1(\underline{k}) = -i\int u p_F \frac{Q}{4\pi}\frac{k_z}{k}\frac{\partial}{\partial k} T\left[\frac{e^{-r/l}}{r^3}\right]$$

$$= -i\int u p_F Q \frac{1}{(2\pi)^3}\frac{k_z}{k}\left(\frac{\tan^{-1}kl}{kl} - 1\right) \qquad (\text{II}.ix.4)$$

We add the contribution $\bar{g}_0(\underline{k})$ from the straight line orbits as in (II.v.16):

$$\bar{g}(\underline{k}) = \frac{\tan^{-1}kl}{kl}\bar{g} + \frac{\alpha^2}{k^2}\left(\frac{\tan^{-1}kl}{kl} - 1\right)\bar{g} - i\int u p_F \frac{Q}{(2\pi)^3}\frac{k_z}{k^2}\left(\frac{\tan^{-1}kl}{kl} - 1\right) \qquad (\text{II}.ix.5)$$

This is the transform of the integral equation for $\nu(r)$ and takes a simple algebraic form, but before we write the solution we compare this equation with one obtained by Peierls in the approximation of a weak charge on the ion. The calculation is repeated in Appendix II and shows that to first order in the charge Ze on the ion:

$$\bar{g}'(\underline{k}) = \frac{\tan^{-1}kl}{kl}\bar{g}' + \frac{\alpha^2}{k^2}\left(\frac{\tan^{-1}kl}{kl} - 1\right)\bar{g}' + i\frac{um}{2\pi^2 p_F}\frac{Ze^2}{k^2+\alpha^2}\,k_z\,\frac{\tan^{-1}kl}{kl} \qquad (\text{II}.ix.6)$$

We note that the first two terms are identical. In the first equation these are the G_0 terms but we cannot yet assert any similar origin for those in the second equation for they have been obtained by a very different method.

The solution to equation (II.ix.5) is:

$$\bar{g}(\underline{k}) = i u \rho_F Q \xi \frac{1}{(2\pi)^3} \frac{k_z}{k^2+\alpha^2} \qquad (II.ix.7)$$

We can immediately derive the inverse transform of this function:

$$\bar{f}(\underline{r}) = \int \bar{g}(\underline{k}) e^{i\underline{k}.\underline{r}} d^3\underline{k}$$

$$= i \xi u \rho_F Q \frac{1}{(2\pi)^3} \int \frac{k_z}{(k^2+\alpha^2)} e^{i\underline{k}.\underline{r}} d^3\underline{k}$$

$$= \xi u \rho_F Q \frac{1}{(2\pi)^3} \frac{\partial}{\partial z} \int \frac{e^{i\underline{k}.\underline{r}}}{k^2+\alpha^2} d^3\underline{k} \qquad (II.ix.8)$$

and this is the transform of a screened Coulomb potential:

$$\bar{f}(\underline{r}) = \xi u \rho_F Q \frac{z}{r} \frac{\partial}{\partial r} \frac{e^{-\alpha r}}{4\pi r}$$

$$f(r) = -\xi u p_p Q \frac{e^{-\alpha r}}{4\pi r^2} \frac{z}{r}(1+\alpha r) \qquad \text{(II.ix.9)}$$

We might now try to evaluate the constant ξ but we can see that the integrals involved in II.ix.3 will diverge near r = o. We cannot use expression II.ix.9 at small r for we have specifically excluded the scattering region from our calculations. We cannot simply extrapolate this function because, as explained in section II.vii, we have exaggerated the density at the ionic origin in our orbit model. We have made approximations which resulted in the factorization of the momentum integrated Green's function and a straightforward Fourier transform. The lower limit on the range of validity of this approximation is not clear. We might consider $r_c = a$ and investigate the importance of the choice in a calculation of the force. At present we have to postpone further discussion of the distribution function until we are better able to understand its behaviour inside the scattering region.

We could improve the Green's function approach by a numerical analysis using the solution to the equations of motion for the orbits. We would begin by solving for the equation of the orbits in a screened Coulomb potential, and use these to calculate the distribution function. This term then contributes to the potential through the Poisson equation and the previous calculation must be repeated with the modified potential. The iteration would, however, involve a long computation and appears quite formidable. So we now turn to investigate another approach to the problem. In

the next chapter we consider an expansion of the distribution function in spherical harmonics. With this method we may obtain some information on the short range behaviour of the distribution function.

CHAPTER III

III.i. The Method of Expansion by Spherical Harmonics

We have seen in Chapter II that the Green's function method is not a tractable form of the Boltzmann equation at short range. The solution within the scattering radius r requires detailed knowledge of the orbit. It is possible to solve the equations of motion in the screened Coulomb potential and use the orbits so obtained in a calculation of the force to first order, if necessary by numerical means. However, we need to know the precise form of the potential V_0 and then we do not know how to solve the integral equation. We are led away from the technique and turn to a method introduced by A.K. Das in his thesis in attempting to solve this problem.

It is plausible at this stage to assume that the distribution function $n_1(\underline{r}, \underline{p})$ is well-behaved in that

it remains finite at the origin, and does not contain any discontinuities. If so, we may find a solution as a series of spherical harmonics in which the first few terms give a good estimate of the behaviour of the function at short range. The simplest method of obtaining the coefficients in this expansion is to substitute the series into the differential equation and, using the orthogonality of the harmonics, multiply the equation so obtained by each of the harmonics and integrate. In the resulting set of equations for the coefficients we have no guide as to how to truncate the expansion for the first few coefficients. This problem is simplified in Das' method by using a variational technique discussed in Ziman (1960). We construct an integral function for which the variational Euler equation is the Boltzmann equation. We insert the harmonic expansion and obtain an Euler equation for each of the harmonics; the variation with respect to each of the coefficients yields a set of first order differential equations in the coefficients of the spherical harmonics. We may then truncate the expansion by solving the Euler equations for the retained harmonics.

The details of this method have been repeated in appendix I. In brief, the variational method demands the construction of an integral I such that $\delta I / \delta n$ is equivalent to the Boltzmann equation $Bn_1 - S = 0$. In general this integral is of the form $I = \frac{1}{2}\tilde{n}_1 B n_1 - \Sigma$ where $\tilde{n}_1$ is orthogonal to n_1 and Σ depends on the form of S. Das takes $\tilde{n}_1 = n_1(r,-p) = n_1^-$. With $n_1(r,p) = n_1^+$ the variational integral that Das derives is:

$$I = \iint d^3\underline{r}\, d^3\underline{p} \left\{ \tfrac{1}{2} n_1^- \left[\underline{v} \cdot \frac{\partial n_1^+}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}} \cdot \frac{\partial n_1^+}{\partial \underline{p}} + \frac{n_1^+}{\tau} \right] \right.$$

$$\left. - \frac{1}{8\pi\tau} \int n_1(\underline{r}, -\underline{p}) n_1^+ d\Omega_{p'} - n_1^- \frac{\partial V_1}{\partial \underline{r}} \cdot \frac{\partial n_0}{\partial \underline{p}} + \frac{mu}{\tau} n_1^- \frac{\partial n_0}{\partial p} \frac{p_z}{p} \right\} \qquad \text{(III.i.1)}$$

In the expansion of $n_1(\underline{r}, \pm\underline{p})$ as a series of products of spherical harmonics the first order differential equation only connects harmonics of order l to $l+1$ and l to $l-1$. The expansion, with $C(l,m)$ derived from the Clebsch-Gordon coefficients, is:

$$n_1(\underline{r}, \pm\underline{p}) = \sum_{l=0}^{\infty} \sum_m C(l,m) \varphi_l(r,p) Y_l^m(\hat{\underline{r}}) Y_{l+1}^{m*}(\hat{\underline{p}})$$

$$\pm \sum_{l=1}^{\infty} \sum_m C(l,m) \psi_l(r,p) Y_l^m(\hat{\underline{r}}) Y_{l-1}^{m*}(\hat{\underline{p}}) \qquad \text{(III.i.2)}$$

We put this function into the variational integral I and consider the variation with respect to the coefficients φ_l and ψ_l to obtain a set of differential equations in those coefficients.

The convergence of such an expansion is fundamental to the technique for the complexity in solving several first order differential equations increases rapidly with the order. In this chapter we shall show that there is no possibility of a rapid convergence at long-range. This does not discourage us in the short-range region where we investigate the first four coefficients. The usual test for convergence is to compare the magnitudes of succeeding terms, but here we are only able to consider the first two terms of each of the series in III.i.2. On general we may often assume that a series has the properties of some geometric

progression, and this can lead to evidence for convergence. But in this case we find that φ_0 and ψ_2 are simply related by the equation of continuity and as such are of the same order of magnitude. Though at first paradoxical this result is understood by considering the equations in the limit of long mean free path. This limit is suggested by a Fourier transform method for weak charge on the ion. Furthermore, the result of this calculation shows, by considering the inverse transform, that the distribution function has a forward-backward asymetry which will require at least the first four harmonics and possibly more.

In his thesis Das considers the variational equations and claims convergence to first order, but later realised his error. With the function χ defined by $V_1 = \frac{ze}{r}\chi(r)$ his first order equations are:

$$-\frac{r^2p^3}{3m}\frac{\partial\psi_1}{\partial r} - \frac{2}{3}\frac{rp^3}{m}\psi_1 + \frac{r^2p^2}{3}\frac{\partial V_0}{\partial r}\frac{\partial\psi_1}{\partial p} - \frac{4\pi}{3\sqrt{3}}r^2p^2\frac{\partial n_0}{\partial p}\left(\frac{\partial\chi}{\partial r}+\frac{2\chi}{r}\right) - \frac{r^2p^2}{\tau}\varphi_0 - \frac{4\pi}{\sqrt{3}}\frac{mu}{\tau}r^2p^2\frac{\partial n_0}{\partial p} = 0 \qquad (\text{III}.i.3a)$$

$$\frac{r^2p^3}{3m}\frac{\partial\varphi_0}{\partial r} - \frac{r^2p^2}{3}\frac{\partial V_0}{\partial r}\frac{\partial\varphi_0}{\partial p} - \frac{2}{3}rp\frac{\partial V_0}{\partial r}\varphi_0 = 0 \qquad (\text{III}.i.3b)$$

These equations offer a simple solution for φ_0 but there is a paradox which was later noticed by Das. This appears when we express the equation of continuity in terms of the spherical harmonics. Since we are looking for stationary solutions to the Boltzmann equation, the equation of continuity takes the form $\operatorname{div}\underline{j} = 0$ and when written out,

becomes:

$$\frac{1}{3}\int_0^\infty \frac{\partial \varphi_0}{\partial r}\, p^3 dp \;+\; \frac{\sqrt{5}}{3}\int_0^\infty \frac{1}{r^3}\frac{\partial}{\partial r}(r^3\psi_2)\, p^3 dp \;=0 \qquad (\text{III}.i.4)$$

This suggests that the ψ_2 term is of the same order as φ_0. As to whether this is important in solving equations (III.i.3) is not clear but it must put the rapid convergence of the harmonics in question. As such we cannot simply adopt the equations (III.i.3) in the hope that their solutions will provide a good approximation to the distribution function.

III.ii Peierls' Fourier Transform method for Weak Charge

We delay further investigation into the variational method until we can understand more about the convergence paradox. We turn to a simpler model in which the charge on the ion as well as its velocity is considered small. Since we expect all the functions to be well-behaved in that any discontinuities will be finite and all singularities integrable, we may Fourier Transform the Boltzmann equation. This is a plausible assumption for we do not expect any singularity to diverge more rapidly than the Coulomb function although this will have to be checked in any solution we derive.

Peierls' transform of the Boltzmann equation is derived in appendix II and we only outline the analysis here. The transform is defined by:

$$g(\underline{q}) = \int e^{i\underline{q}\cdot\underline{r}}\, f_1(\underline{r})\, d^3\underline{r} \qquad (\text{III}.ii.1)$$

and the Boltzmann equation takes the form:

$$\frac{i}{m}(\underline{p}\cdot\underline{k})g(\underline{p},q) - i\int d^3q' q' \frac{\partial}{\partial p} g(\underline{p}, \underline{k}-\underline{q}')V_0(q') + \frac{1}{\tau}(g-\bar{g}) = -\frac{u}{\tau} p_z \delta(q) + \frac{i}{m}(\underline{p}\cdot\underline{q})V_1(q) \qquad (\text{III}.ii.2)$$

If we linearize the function g in the charge Ze the zero order solution is:

$$g_0 = -up_z\delta(q) \qquad (\text{III}.ii.3)$$

This is theundisturbed electron distribution function in the moving frame of the ion. It is the Fourier Transform of the function in equation (II.i.17) due to a transformation into the moving frame of the ion, but of zero order in its charge.

When we linearize the potential terms we have

$V_{00} = V_{01} = 0$ for the zero order in the charge.

V_{10} is taken to be the screened Coulomb potential though we shall see later that this is not a good choice close to the ion; V_{11} is related to the solution g_1 through the Poisson equation:

$$V_{11} = -\frac{\alpha^2}{q^2}\bar{g}_1 \qquad (\text{III}.ii.4)$$

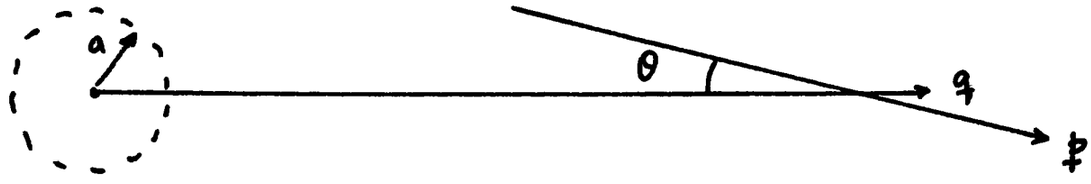
The equation for g_1 is then:

$$g_1 = \frac{1}{\left(\frac{i}{m}(\underline{p}\cdot\underline{q}) + \frac{1}{\tau}\right)}\left\{\left(-\frac{i}{m}\alpha^2\frac{\underline{p}\cdot\underline{q}}{q^2} + \frac{1}{\tau}\right)\bar{g}_1 + \frac{iuq_z}{2\pi^2}\frac{Ze^2}{\alpha^2+q^2}\right\} \qquad (\text{III}.ii.5)$$

from which $\bar{g}_1$ is obtained by direct integration:

$$\bar{g}_1 = i\frac{Ze^2}{2\pi^2}u\tau q_z \frac{q^2}{(q^2+\alpha^2)^2}\frac{\tan^{-1}ql}{ql-\tan^{-1}ql} \qquad (\text{III}.ii.6)$$

We are already able to recognise a feature of this function g_1 . The denominator of (III.ii.5) contributes a singularity which depends on the angle between the momentum $\underline{p}$ and the wave-vector $\underline{q}$. This is significant at large distances from the ion where a small change in the direction of $\underline{p}$ has a large effect on the history of the electron.



The contribution at radius $\sim l$ the mean free path will only contain electrons scattered off the ion in an angular region $\theta \leq a/l$. This critical dependence on the vector $\underline{p}$ suggests already that at least for long range, a spherical harmonic expansion will not converge rapidly, though it may still be of use at short range.

III.iii The Long Mean Free Path Limit

This expression for $\bar{g}_1$ contains the limitation of not being applicable at short range, or large q where the inverse transform is clearly diverging logarithmically. It assumes more significance, however, when considered in the light of a quantum mechanical calculation. The large values of q are physically suppressed by momentum conservation. The momentum transferred to the ion cannot be greater than twice the Fermi momentum. This corresponds to the direct

collision in which the electron is scattered back along its own path. Later on, in chapter IV, we consider the quantum mechanics of the system and derive an expression for the Fourier transform of the charge density which is similar to the expression (III.ii.6) but includes the cut-off criterion:

$$q \leq 2k_F$$

A further point demonstrated by the quantum mechanical calculation is in regard to the mean free path of the electron. For it assumes ab initio that the scattering of the electrons close to the ion is independent of the mean free path. In this region the electrons are so much more likely to scatter off the ion than off any other impurity or off the lattice that the probability of the latter occurring is negligible.

The result of this latter calculation differs from the Fourier Transform result in that the factor

$$\tan^{-1}ql \,/\, ql - \tan^{-1}ql$$

is replaced by its asymptotic value $\pi/2ql$. So we see that taking the limit $l \to \infty$ subsequent to the classical calculation yields the same result as in a quantum calculation where this limit was taken initially. It is a common feature of these calculations that the charge on the ion is considered to be small.

The success of this $l \to \infty$ approximation in connecting classical and quantum solutions leads us to look again at the harmonic analysis. This method does not involve the approximation of weak charge on the ion, and provided a tractable form for the equations may be found, should improve on the other calculations. If we look first at the equations to order $\psi_1 \phi_0$ we see that if we can ignore terms to order $\frac{1}{\tau}$ then the first equation

becomes a first order homogeneous differential equation, relating ψ_1 and the potential term χ. If $\{\psi_1\}$ denotes some function of ψ_1 equation (III.i.3)is:

$$\{\psi_1\} + \frac{\varphi_0}{\tau} = \{\chi\} + \{\tfrac{1}{\tau}\} \qquad (\text{III.ii.1})$$

Now the Poisson equation has not been used to derive this expression. We can immediately see that the two equations do not allow for any non-zero solutions for the potential χ even at short range.

We next look at the second order equations, and then find, in the same prescription, the four equations:

$$\begin{aligned} \{\psi_1\} + \{\varphi_1\} + \frac{\varphi_0}{\tau} &= \{\chi\} + \{\tfrac{1}{\tau}\} \\ \{\psi_1\} - \{\varphi_1\} + \frac{\psi_2}{\tau} &= \{\chi\} \\ \{\varphi_0\} + \{\psi_2\} &= \{V_0\} \\ \{\varphi_0\} - \{\psi_2\} &= \{V_0\} \end{aligned} \qquad (\text{III.ii.2})$$

We can now see in this $t \to \infty$ limit that the terms contributing most to χ are ψ_1 and φ_1 and that φ_0 and ψ_2 may indeed be of the same order of magnitude, but do not necessarily contribute to χ.

Whilst this approximation helps us to understand the paradox over the continuity equation we are no nearer a

useful test for the convergence of this harmonic series. Even if $\varphi_0 > \varphi_1$ we cannot determine that $\psi_1 > \psi_2$ and indeed this looks unlikely. We cannot rule out that the higher terms will rapidly converge, after all we know that the solution for ψ_1 that we seek must be well-behaved near the origin if we are to solve the Poisson equation. At this stage we cannot assert that the variational coefficients φ_0 φ_1, ψ_1, ψ_2 are sufficient.

We may persue this line of approach by obtaining equations including the third order coefficients φ_2 and ψ_3 and looking for criteria to determine their magnitude. However the derivation of the equations to this order will be lengthy and even then we may not be able to obtain a satisfactory solution analytically. We have used all the simple relations such as the equation of continuity which might yield criteria for convergence. We now leave this formidable task in favour of a more direct approach. We can assert that if the harmonic expansion does not converge rapidly for small values of the ionic charge then it will not do so for any larger value. We investigate the inverse transform of the function g_1 of equation (III.ii.5) with this convergence in mind.

III.iv The Inverse Transform of g_1.

The solution near the origin that we seek is still going to arise in the $\tau \longrightarrow \infty$ limit and we only retain $1/\tau$ as the small quantity ϵ to indicate the irreversibility. This term shows that the scattered particles follow from the incoming ones; mathematically it will indicate the direction of integration round a singularity.

We look first at the inverse transform of $\bar{g}_1 \frac{\alpha^2}{q^2}$ with $\bar{g}_1$ given by equation (III.ii.6). This is reduced to a complex integral over the radial component of q. The integral is separated into four terms which are integrated over contours parallel to the imaginary axis. By completing these contours we are able to express the integral in terms of the exponential integral function (see Jahnke and Emde : Funktionentafeln 1933). This is defined by: or (1945)

$$-Ei(-x) = \int_x^\infty \frac{e^{-t}}{t}\,dt \qquad \text{for} \quad 0 < x < \infty$$

and $$\overline{Ei}(x) = Ei^+(x) + i\pi = Ei^-(x) - i\pi = \tfrac{1}{2}\left(Ei^+(x) + Ei^-(x)\right) \qquad (\text{III}.iv.1)$$

where $$Ei^-(x) = Ei\left(-x\,e^{i\pi}\right) = Ei(x - i0)$$

$$Ei^+(x) = Ei\left(-x\,e^{-i\pi}\right) = Ei(x + i0)$$

The second term in the inverse transform of g_1 is analysed by writing the integrand in a spherically symmetric form relative to the q coordinates. We orientate the system about the vectors $\underline{p}$ and $\underline{r}$ and integrate the function in rectangular coordinates.

The first term in the transform is:

$$\int -\frac{\alpha^2}{q^2}\bar{g}_1\, e^{-i\underline{q}\cdot\underline{r}}\,d^3\underline{q} = -i\,\frac{Ze^2}{4\pi}\,\alpha^2\,\frac{u}{v}\int q\,dq\int d\omega\, e^{-i\underline{q}\cdot\underline{r}}\,\frac{q_z}{(q^2+\alpha^2)^2}$$

$$= \frac{Ze^2}{4\pi}\,\alpha^2\,\frac{u}{v}\,\frac{\partial}{\partial z}\left(\frac{-1}{2\alpha}\right)\frac{\partial}{\partial\alpha}\int_0^\infty \frac{q\,dq}{q^2+\alpha^2}\int_{-1}^{1} d(\cos\theta)\,2\pi\, e^{-iqr\cos\theta}$$

$$= \frac{Ze^2}{2}\,\alpha^2\,\frac{u}{v}\,\frac{\partial}{\partial z}\left(\frac{i}{2\alpha r}\right)\frac{\partial}{\partial\alpha}\int_0^\infty dq\;\frac{e^{iqr} - e^{-iqr}}{q^2+\alpha^2} \qquad (\text{III}.iv.2)$$

We use the identity:

$$\frac{1}{q^2+\alpha^2} = -\frac{1}{2i\alpha}\left\{\frac{1}{q+i\alpha} - \frac{1}{q-i\alpha}\right\} \qquad (\text{III}.\text{iv}.3)$$

to write:

$$\int_0^\infty dq\, \frac{e^{iqr} - e^{-iqr}}{(q^2+\alpha^2)} = -\frac{1}{2i\alpha}\int_0^\infty dq \left\{ \frac{e^{i(q+i\alpha)r}}{q+i\alpha}e^{\alpha r} - \frac{e^{-i(q+i\alpha)r}}{q+i\alpha}e^{-\alpha r} - \frac{e^{i(q-i\alpha)r}}{q-i\alpha}e^{-\alpha r} + \frac{e^{-i(q-i\alpha)}}{q-i\alpha}e^{\alpha r}\right\}$$

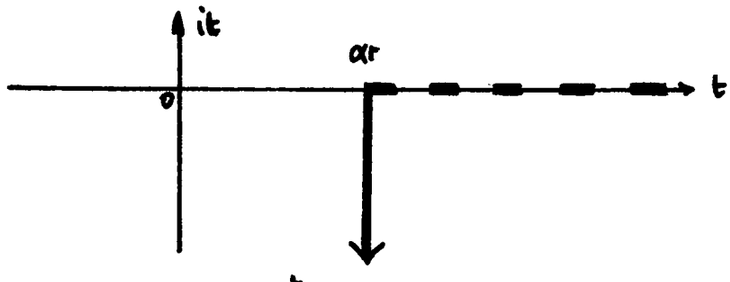
$$(\text{III}.\text{iv}.4)$$

Consider the term $\int_0^\infty dq\, \frac{e^{i(q+i\alpha)r}}{q+i\alpha}$

and let $t = -i(q+i\alpha)r$

So that we have $\int_{\alpha r}^{-i\infty} \frac{e^{-t}}{t}\, dt$

In the complex t-plane:



The function $e^{-t}/t \longrightarrow 0$ as $|t| \to \infty$ so we may change the path of integration to

$$\alpha r < t < \infty$$

with no further contribution from $-i\infty < t < \infty$

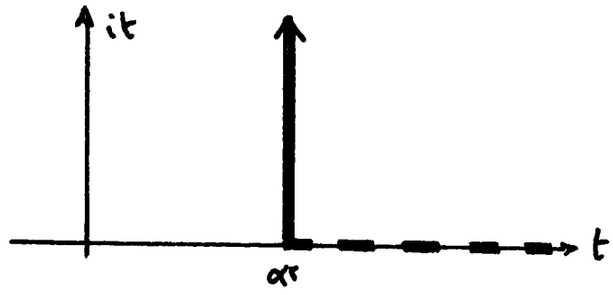
Then:

$$\int_0^\infty dq\, \frac{e^{i(q+i\alpha)r}}{q+i\alpha} = \int_{\alpha r}^\infty \frac{e^{-t}}{t}\, dt = -Ei(-\alpha r) \qquad (\text{III}.\text{iv}.5)$$

Similarly

$$\int_0^\infty dq\, \frac{e^{-i(q-i\alpha)r}}{(q-i\alpha)} = \int_{\alpha r}^{i\infty} \frac{e^{-t}}{t}\, dt = \int_{\alpha r}^{\infty} \frac{e^{-t}}{t}\, dt = -Ei(-\alpha r) \qquad (\text{III}.\text{iv}.6)$$

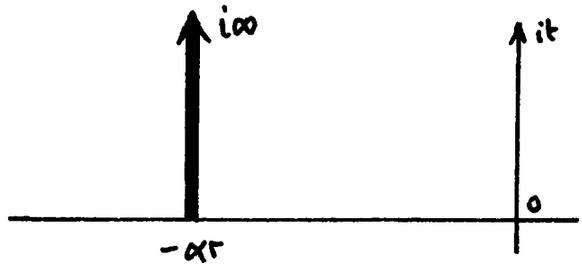
In this case, the path of integration in the complex t-plane is:



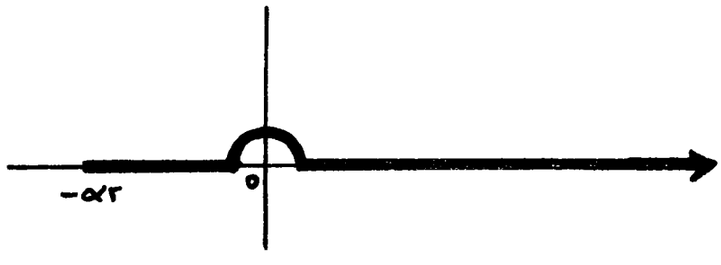
The contribution from the term $\int_0^\infty dq \; \frac{e^{-i(q+i\alpha)r}}{q+i\alpha}$ is transformed by $t = i(q+i\alpha)r$ to

$$\int_{-\alpha r}^{i\infty} \frac{e^{-t}}{t}\, dt$$

and in the complex t-plane this path of integration is:



We again use the property of $e^{-t}/t \to 0$ as $|t| \to \infty$ to change the path of integration to one along the real axis, but now have to note that there is a pole at the origin, which must be excluded from the contour $-\alpha r \to \infty \to i\infty \to -\alpha r$ The final path of integration then becomes:



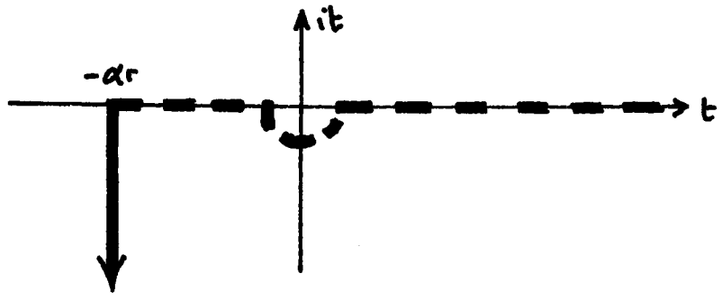
to give

$$\int_0^\infty dq \; \frac{e^{-i(q+i\alpha)r}}{q+i\alpha} = \int_{-qr+i0}^{\infty} pp \; \frac{e^{-t}}{t}\, dt + i\pi = -Ei(\alpha r) \qquad (\text{III}.iv.7)$$

Similarly

$$\int_0^\infty dq \; \frac{e^{i(q-i\alpha)r}}{q-i\alpha} = \int_{-\alpha r-i\infty}^{\infty} \mathrm{pp}\, \frac{e^{-t}}{t}\, dt \; - i\pi \quad = \quad -\bar{Ei}(\alpha r)$$

where the paths of integration in the complex t-plane are:



Then

$$\int_0^\infty dq \; \frac{e^{iqr} - e^{-iqr}}{(q^2+\alpha^2)} = \frac{1}{2i\alpha}\left\{2e^{\alpha r} Ei(-\alpha r) - 2e^{-\alpha r}\bar{Ei}(\alpha r)\right\} \qquad (\text{III}.iv.8)$$

and

$$T\left[-\frac{\alpha^2}{q^2}\bar{g}_1\right] = \frac{Ze^2}{4}\frac{u}{v}\alpha^2\frac{z}{r}\frac{\partial}{\partial r}\frac{1}{\alpha r}\frac{\partial}{\partial \alpha}\frac{1}{\alpha}\left\{e^{\alpha r}Ei(-\alpha r) - e^{-\alpha r}\bar{Ei}(\alpha r)\right\}$$

We use the identity $\dfrac{\partial}{\partial y}\displaystyle\int_{f(y)}^{b} g(x)\,dx = -\frac{\partial f}{\partial y}g(f)$

to show $\dfrac{\partial}{\partial r}Ei(-\alpha r) = \dfrac{e^{-\alpha r}}{r}$ & $\dfrac{\partial}{\partial r}\bar{Ei}(\alpha r) = \dfrac{e^{\alpha r}}{r}$

The differentiation is then straightforward and yields: (III.iv.9)

$$T\left[-\frac{\alpha^2}{q^2}\bar{g}_1\right] = \frac{u}{4v}Ze^2\alpha^2\frac{z}{\alpha^3r^3}\left\{2\alpha r + (1-\alpha r+\alpha^2r^2)e^{\alpha r}Ei(-\alpha r) - (1-\alpha r-\alpha^2r^2)e^{-\alpha r}\bar{Ei}(\alpha r)\right\}$$

We note that this term, which corresponds to the potential V_1, varies as $\ln(\alpha r)$ for small distances. This singularity arises from the classical screening approximation which is strictly not valid at such short radii, as will be demonstrated in the quantum mechanical calculation.

The second term in the transform is given by:

$$\frac{um\,Ze^2}{2\pi^2}\int d^3q\; e^{i\underline{q}\cdot\underline{r}}\frac{q_z}{(q^2+\alpha^2)(\underline{p}\cdot\underline{q}-i\epsilon)} = \frac{um\,Ze^2}{2\pi^2}(-i)\frac{\partial}{\partial z}\int d^3q\;\frac{e^{i\underline{q}\cdot\underline{r}}}{(q^2+\alpha^2)(\underline{p}\cdot\underline{q}-i\epsilon)} \qquad \text{(III.iv.10)}$$

The factors in the integrand are now not related to any coordinates of $\underline{q}$ so we are free to choose $\underline{p} = (0, 0, p)$ and then define the x axis such that the xz-plane contains both vectors $\underline{r}$ and $\underline{p}$. Then $\underline{r} = (x, 0, z)$ and:

$$I = \int_{-\infty}^{\infty} dq_x\, dq_y\, e^{iq_x x}\int_{-\infty}^{\infty} dq_z\;\frac{e^{iq_z z}}{(q_z^2+\sigma^2+\alpha^2)(q_z p-i\epsilon)} \qquad \sigma^2 = q_x^2+q_y^2$$

This integral has simple poles at $q_z = \pm i\sqrt{\sigma^2+\alpha^2}$, $+i\epsilon$. The value of this integral then depends on whether $z>0$ or $z<0$ since we must close the contour such that $iq_z z \to -\infty$ as $q_z \to \infty$. If $z>0$ we close the contour in the upper half-plane and pick out the residues at the poles $i\epsilon$ and $+i\sqrt{\sigma^2+\alpha^2}$ to give:

$$I = \int_{-\infty}^{\infty} dq_x\, dq_y\, e^{iq_x x}\left\{\frac{1}{p}\frac{2\pi i}{(q_x^2+q_y^2+\alpha^2)} + \frac{2\pi}{p}\;\frac{e^{i\sqrt{\sigma^2+\alpha^2}\,z}}{2(q_x^2+q_y^2+\alpha^2)}\right\} \;:\; z>0$$

and if $z < 0$ then we close the contour in the lower half-plane and pick out only the residue at the pole $-i\sqrt{\sigma^2+\alpha^2}$ to give:

$$I_0 = \int_{-\infty}^{\infty} dq_x\, dq_y\, e^{iq_x x} \quad \frac{2\pi}{\beta} \quad \frac{e^{-i\sqrt{\sigma^2+\alpha^2}\,z}}{2(q_x^2+q_y^2+\alpha^2)} \qquad : \qquad z<0$$

Considering first the integral $z<0$

$$I_0 = \int_0^{\infty} q\,dq \int_0^{2\pi} d\theta\, e^{iqx\cos\theta} \quad \frac{2\pi}{\beta} \quad \frac{e^{-i\sqrt{q^2+\alpha^2}\,z}}{2(q^2+\alpha^2)}$$

With the integral representation for a Bessel function

$$I_0 = \frac{2\pi^2}{\beta} \int_0^{\infty} dq\; q \quad \frac{e^{-i\sqrt{q^2+\alpha^2}\,z}}{(q^2+\alpha^2)} \quad J_0(qx) \qquad (\text{III}.\text{iv}.11)$$

This expression is at least well-behaved away from the origin. The term of more interest to a spherical harmonics expansion is that which appears for $z>0$. This is given by:

$$I_1 = \int_{-\infty}^{\infty} dq_x\, dq_y\, e^{iq_x x} \quad \frac{2\pi i}{\beta} \quad \frac{1}{(q_x^2+q_y^2+\alpha^2)}$$

$$= \frac{2\pi i}{\beta} \int_0^{\infty} q\,dq \quad \frac{1}{(q^2+\alpha^2)} \int_0^{2\pi} e^{ixq\cos\theta}\, d\theta$$

$$= \frac{2\pi i}{\beta} \int_0^{\infty} dq \quad \frac{q}{(q^2+\alpha^2)} \quad J_0(qx)$$

since $J_0(qx) = \frac{1}{\pi}\int_0^{2\pi} e^{iqx\cos\theta}\,d\theta$

The integral is finally given in terms of the Bessel function of the second kind with complex argument:

$$I_1 = \frac{2\pi^2 i}{p} K(\alpha x) \qquad (\text{III}.iv.12)$$

We now generalise x to a vector perpendicular to p: $\frac{|\underline{r}\wedge\underline{p}|}{p} = \frac{|\underline{L}|}{p}$

and the contribution to $\bar{f}_1$ is:

$$\frac{um\,Ze^2}{p}\frac{\partial}{\partial z} k_0\left(\frac{\alpha L}{p}\right)$$

We are now able to see that the function n_1, the inverse transform of g_1 has some sort of singularity at $z = 0$ the coordinate chosen above. This represents an asymetry between forward and backward terms in r and shows that we shall need harmonics at least to the order containing φ_0 φ_1 ψ_1 ψ_2 . It is the dipole term which will give the first approximation to such an asymmetry. The significance of the higher order term will depend on the nature of the singularity. We note that g_1 is sufficiently well-behaved for the Fourier Transform to exist.

In this chapter we have investigated the method of expansion by spherical harmonics with a view to obtaining a solution at short range. Although Das has already obtained a first order solution in this region in the approximation of weak ionic charge he was incorrect on the important matter of convergence of the coefficients. We have been able to understand some of the problems, particularly the paradox

over the equation of continuity, by looking at the approximation of long mean free path. Physically this is interpreted as meaning that near the ion the electrons are so much more likely to scatter off the ion than off any other impurity, electron, or lattice that the latter may be neglected. Although useful in explaining the paradox this approximation could not be used to obtain any definite criteria for the convergence of the coefficients. It was only by considering the Fourier Transform for weak charge that we obtained more detailed information. The inverse transform has shown a distinct asymetry and possibly a more serious singularity in the distribution function, and this would require evaluation of harmonics at least to second order. Even then we cannot be sure that these terms will give a good approximation to the distribution function and further evaluation is a formidable task.

We return in the next chapter to the approximation of long-mean free path that we used in section III.iii to investigate the form of Das' equations near the origin. This does remove a parameter from the equations and in the simplified form we tackle the problem with a quantum mechanical analysis. We have discussed some of the results in earlier sections, particularly the similarity with the solution by the Fourier Transform method, but the cut-off will prove to be of more interest.

CHAPTER IV

IV.i The Ionic Potential as a Perturbation

In attempting a spherical harmonics expansion to solve the Boltzmann equation at short range we were looking for a solution to first order in the ionic velocity but with no such limitation on the charge on the ion. We were unable to deduce a criterion for convergence for the expansion. The only contribution towards such a criterion, that from the equation of continuity, led to a paradoxical ordering of the coefficients. We were able to understand this paradox by considering the Fourier Transform method for a weak charge on the ion, though we were still unable to establish any general criterion for convergence.

The result of this weak charge calculation is of further interest. We considered the transport equation in momentum space by means of the Fourier Transform. The ionic potential was taken to be the classical screened Coulomb

potential, and this yielded a logarithmic divergence at the origin in the distribution function. The final step, that of deriving the inverse transform, is not however a rigorous step as the classical screened Coulomb potential only applies in the limit of $k \ll k_F$. In this chapter we investigate the form of thepotential beyond this limit in a quantum mechanical calculation. We maintain the infinite mean free path model used in explaining the harmonic paradox for it appears to be useful in describing the motion of the electrons close to the ion.

In a quantum mechanical analysis for small ion velocity we should solve the Schrödinger equation for the electron wave functions in the presence of a screened Coulomb potential and then add the velocity dependent potential as a perturbation. It is, however, useful in understanding some aspects of the problem to consider the ionic potential itself as a perturbation, by making the approximation of weak charge. The unperturbed Hamiltonian is then just the kinetic term. The value of this analysis lies in the appearanc of a cut-off in the allowed k values, and we shall use this to obtain a solution to the Green's function analysis of Chapter II when we consider the force on the ion in the last chapter.

We construct a density matrix formalism following C. Kittel (1963). The term to first order in the ionic velocity ρ_1 is related to the velocity dependent potential by the Poisson equation. By considering the equation of motion of the density matrix we are able to derive an expression for the "self-consistent potential". This result is simply related to Lindhard's expression for the dielectric constant discussed in Ziman (1964).

The advantage of using a density matrix formalism lies in the description of the unperturbed metal as a set of states rather than any one. The scattering process is an essential feature of conduction in a metal; without it the electrons are accelerated indefinitely in the external field. This process cannot be described in terms of a single state.

We make use of Das' result that the external field is equivalent to an increase in the ionic velocity. We calculate the form of the moving potential in the frame of the electrons by relating the velocity dependence to the frequency ω in a Fourier transform. There is then a simple transformation into the frame of the ion. In the $\omega \rightarrow 0$ or $u \rightarrow 0$ limit we obtain in section IV.ii the textbook results: (i) if the momentum transfer $q << k_F$ we have the screened Coulomb potential, (ii) for more general q we derive the usual q dependence of the screening parameter α which exhibits the Kohn effect. In section IV.iii we consider the velocity dependent term of Lindhard's expression. The integrand is expressed in terms of a principal part and a pole. The principal part integral is shown to have no contribution to first order in the velocity. The pole contributes a term equal to the classical expression from Peierl's Fourier Transform method in the limit of long mean free path. The condition for the pole to exist is approximately

$$q < 2k_F .$$

The result of the calculation for the potential is similar to that obtained by many-body techniques. We are able to introduce a connection between the frequency ω in the Fourier transform and the ionic velocity u . The more general expression has been derived by Dubois (1959). In his paper the method of Gell-Mann and Brueckner for treating electron interactions in a degenerate electron gas is

generalised using the Feynman-Dyson techniques of field theory. Our expression for α^2 then appears as the propagator for density fluctuations in the electron field. The sum of those interaction terms represented by polarization loops in the diagrammatic method yields the same expression for the dielectric susceptibility. It has already been suggested (Kittel p.124) that this method will give the same results as the S.C.F. method. Since we do not calculate the corrections from other diagrams we confirm the result by the S.C.F. method. The corrections will come from the electron interaction which prevents the charge accumulating at the ion and giving a divergent electron density. To include this effect we may have to turn to the diagrammatic method and look for the dominant terms as $q \rightarrow \infty$. In this case the polarization loops will be negligible at each order and some other resummation will be required. We should then have to answer the question as to whether any perturbation expansion is valid at $q \rightarrow \infty$ for then the Coulomb energy will be greater than the unperturbed kinetic energy.

The single-particle Hamiltonian may be written:

$$\mathcal{H} = H_0 + V_0 + V_u \qquad (\overline{IV}.i.1)$$

where H_0 is the kinetic term $p^2/2m$, V_c is a moving Coulomb potential given by:

$$V_c(\underline{r},t) = \int V'(\underline{r}') \, \delta(\underline{r}' - \underline{r} + \underline{u}\,t) \, d^3\underline{r}' \qquad (\overline{IV}.i.2)$$

$$V'(\underline{r}') = \frac{Ze^2}{r}$$

and V_u is the velocity dependent correction. Let $V = V_c + V_u$ be the "self-consistent" potential. In the unperturbed Hamiltonian the states of the electrons may be characterized by their wave-vectors $\underline{k}$. We define a density matrix ρ_0 in the unperturbed Hamiltonian such that

$$\rho_0 \, |\underline{k}\rangle = f_0(k) \, |\underline{k}\rangle \qquad (\underline{IV}.i.3)$$

where $f_0(k)$ is the Fermi-Dirac distribution function describing the free-electron distribution in a metal. The effect of the ion is to introduce a correction term ρ_1 to the density matrix. The equation of motion of the density matrix is:

$$i \frac{\partial \rho}{\partial t} = [\mathcal{H}, \rho] = [H_0, \rho_0] + [H_0, \rho_1] + [V, \rho_0] \qquad (\underline{IV}.i.4)$$

where we have neglected terms to order $[V, \rho_1]$

We now solve this equation of motion for the ρ_1 density matrix and solve the Poisson equation for the correction to the potential due to screening and drift of the electron gas in terms of ρ_1 :

$$-q^2 V_u(q,\omega) = -4\pi e^2 \sum_k \langle \underline{k} | \rho_1(\omega) | \underline{k}+\underline{q} \rangle \qquad (\underline{IV}.i.5)$$

Since the unperturbed state is stationary:

$$i \frac{\partial \rho_0}{\partial t} = [H_0, \rho_0] = 0$$

We take matrix elements of equation (IV.i.4) between states $|\underline{k}\rangle$ and $|\underline{k}+\underline{q}\rangle$ to give an equation of motion

for ρ_1 :

$$i\frac{\partial}{\partial t}\langle \underline{k}|\rho_1|\underline{k}+\underline{q}\rangle = \langle \underline{k}|[H_0,\rho_1]|\underline{k}+\underline{q}\rangle + \langle \underline{k}|[V,\rho_0]|\underline{k}+\underline{q}\rangle$$

$$= \left(\varepsilon_k - \varepsilon_{k+q}\right)\langle \underline{k}|\rho_1|\underline{k}+\underline{q}\rangle + \left\{f_0(\underline{k}+\underline{q}) - f_0(\underline{k})\right\} V(q,t) \qquad (\underline{IV}.i.6)$$

we complete the transform of $V(q,\omega)$ including a factor e^{st} which in the limit $s \to 0$ serves to switch on the potential adiabatically:

$$V(q,\omega) = \int V(q,t)\, e^{i\omega t} e^{st}\, dt$$

Then ρ_1 will have the same time dependence and we may write equation (IV.i.6):

$$\left(\varepsilon_{k+q} - \varepsilon_k - \omega + is\right)\langle \underline{k}|\rho_1|\underline{k}+\underline{q}\rangle = \left\{f_0(\underline{k}+\underline{q}) - f_0(\underline{k})\right\} V(q,\omega)$$

which with the Poisson equation (IV.i.5) gives:

$$V_u(q,\omega) = \frac{4\pi e^2}{q^2} \sum_{\underline{k}} \frac{f_0(\underline{k}+\underline{q}) - f_0(\underline{k})}{\varepsilon_{k+q} - \varepsilon_k - \omega + is}\, V(q,\omega)$$

The self-consistent potential is $V(q,\omega) = V_c + V_u$

$$V(q,\omega) = \left\{1 - \frac{4\pi e^2}{q^2}\int \frac{d^3\underline{k}}{(2\pi)^3} \frac{f_0(\underline{k}+\underline{q}) - f_0(\underline{k})}{\varepsilon_{k+q} - \varepsilon_k - \omega + is}\right\}^{-1} V_c(q,\omega) \qquad (\underline{IV}.i.7)$$

The factor in brackets is the Lindhard expression for the dielectric constant of this electron gas.

We cannot include the external field directly in

the calculation as we have neglected the scattering mechanism which prevents the indefinite acceleration of the electrons. But we have used in chapter II the result of Das that the external field is equivalent to an increase in the ion velocity to u . The Fourier Transform of the moving Coulomb potential (II.i.2) is:

$$V_c(q,\omega) = \int e^{i(q\cdot r - \omega t)} V'(r') \, \delta(r' - r + ut) \, d^3r' \, d^3r \, dt$$

$$= \int e^{i[q\cdot r' - (\omega - q\cdot u)t]} V'(r') \, d^3r' \, dt$$

$$= V'(q) \int e^{-i(\omega - q\cdot u)t} \, dt$$

where $V'(q)$ is the transform of the stationary Coulomb potential:

$$V_c(q,\omega) = \frac{Ze^2}{2\pi^2} \frac{1}{q^2} \delta(\omega - q\cdot u) \qquad (IV.i.8)$$

with $u = u_z = u$ the self-consistent potential of equation (IV.i.7) is:

$$V(q,\omega) = \frac{Ze^2}{2\pi^2} \delta(\omega - q\cdot u) \left\{ q^2 - \frac{4\pi e^2}{(2\pi)^3} \int d^3k \, \frac{f_0(k+q) - f_0(k)}{\varepsilon_{k+q} - \varepsilon_k - \omega + is} \right\}^{-1}$$

We use the identity: $V(\omega)\delta(\omega - q\cdot u) = V(q_z u)\delta(\omega - q_z u)$

and omit the factor $\delta(\omega - q_z u)$ from this expression as it will just transform the stationary $V(q)$ into the moving frame of the ion. In that frame:

$$V(q) = \frac{Ze^2}{2\pi^2} \frac{1}{q^2+\alpha'^2} \qquad (\underline{IV}.i.9)$$

where

$$\alpha'^2 = -\frac{4\pi e^2}{(2\pi)^3} \int d^3\underline{k} \; \frac{f_0(\underline{k}+\underline{q}) - f_0(\underline{k})}{\varepsilon_{k+q} - \varepsilon_k - u q_z + is} \qquad (\underline{IV}.i.10)$$

This is an effective screening parameter by analogy with the classical screening potential

$$V_{cl.}(\underline{r}) = Ze^2 \frac{e^{-\alpha r}}{r}$$

$$V_{cl}(q) = \frac{Ze^2}{2\pi^2} \frac{1}{q^2+\alpha^2}$$

IV.ii The Stationary Potential

In this section we evaluate the expression (IV.i.10) for α'^2 with $u=0$. In a metal at normal temperatures we may consider the Fermi-Dirac distribution function at zero temperature; then f_0 is a hard sphere of radius k_F, the Fermi momentum. The factor $f_0(\underline{k}+\underline{q}) - f_0(\underline{k})$ is now the difference between two such spheres whose centres are separated by the vector q as in Figure IV.1.

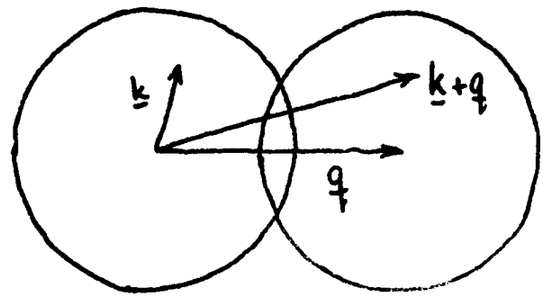


Fig. $\underline{IV}$.1

The integral may be written, with $\underline{k}+\underline{q}=\underline{k}'$

$$\alpha'^2(u=0) = \frac{4\pi e^2}{(2\pi)^3}\left\{\int_{k<k_F} d^3\underline{k}\ \frac{1}{(\underline{k}+\underline{q})^2/2m - k^2/2m + is} - \int_{k'<k_F} d^3\underline{k}\ \frac{1}{k'^2/2m - (\underline{k}'-\underline{q})^2/2m + is}\right\} \qquad (\text{IV}.\text{ii}.1)$$

We choose the vector $\underline{q}$ to lie along the z - axis of the k integration. With $\underline{k}.\underline{q} = kq\cos\theta$ we have:

$$\alpha'^2(u=0) = \frac{8\pi^2e^2}{(2\pi)^3}\frac{m}{q}\left\{\int_0^{k_F}k^2dk\int_{-1}^{1}d(\cos\theta)\ \mathcal{P}\frac{1}{k\cos\theta + q/2} - \int_0^{k_F}k'^2dk'\int_{-1}^{1}d(\cos\theta)\ \mathcal{P}\frac{1}{k'\cos\theta - q/2}\right\} \qquad (\text{IV}.\text{ii}.2)$$

We have used the identity

$$\lim_{s\to 0}\frac{1}{x+is} = \mathcal{P}\frac{1}{x} - i\pi\delta(x)$$

and ignored the pole. We shall show in the next section that there is no contribution from the pole if $u=0$ The $\cos\theta$ integration is straightforward:

$$\alpha'^2(0) = \frac{\alpha^2}{2k_Fq}\left\{\int_0^{k_F}k\,dk\,\ln\left|\frac{1+q/2k}{1-q/2k}\right| - \int_0^{k_F}k'dk'\,\ln\left|\frac{1-q/2k'}{1+q/2k'}\right|\right.$$

The integrands are now identical and additive. Using the result:

$$\int k\,dk\, \ln|k+a| = \frac{k^2-a^2}{2}\ln|k+a| - \frac{k^2}{2} + \frac{ak}{2} \qquad (\text{IV}.ii.4)$$

we obtain the result quoted in Ziman (1964):

$$\alpha'^2(q,u=0) = \frac{\alpha^2}{2}\left\{1 + \frac{4k_F^2-q^2}{4k_Fq}\ln\left|\frac{2k_F+q}{2k_F-q}\right|\right\} \qquad (\text{IV}.ii.5)$$

with α^2 given by its classical value: $\alpha^2 = \frac{32\pi^2 e^2 m k_F}{(2\pi)^3}$

Graphically:

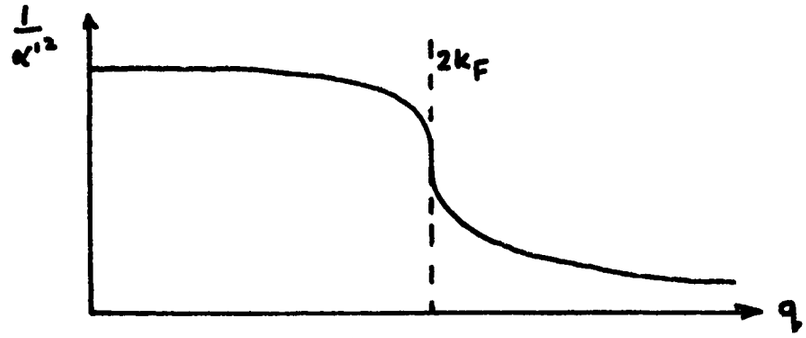


Fig. IV.2

There are two points of interest in this result. For large values of q the screening parameter α'^2 varies as α^2/q^2. This shows that as the electrons move nearer the ion ($q \longrightarrow \infty$) the effective screening parameter increases and the effective potential returns to the Coulomb form. The cross-over occurs rapidly near the value $q = 2k_F$ which is close to the inverse classical screening radius $1/a$. This supports the form of the potential seen by the moving electrons used in the long-range solution of chapter II:

$$V_{eff}(r) = \begin{cases} \frac{Ze^2}{r} & r < a \\ \text{negligible} & r > a \end{cases}$$

The second aspect of the form of α'^2 is the singularity at $q = 2k_F$ for we shall obtain a similar singularity in the velocity dependent term. The function is everywhere finite and continuous, varying as $x \ln x$ for $x \to 0$ in this region, but has a divergent derivative. This behaviour is used to explain the Kohn effect in the phonon spectrum. It may be understood in terms of the Fermi spheres of Figure IV.1 for $q = 2k_F$ corresponds to the two spheres just touching. Up to this value of q an increase will make available more final scattering states. Beyond this value the spheres do not overlap, no more states are made available, and the integral tends to the inverse square of their separation.

IV.iii The Velocity-dependent Potential

We return to expression (IV.i.10) for α'^2 and using the identity (IV.ii.3) separate the integrand into its principal part and the pole. Once more we write $\underline{k}' = \underline{k} + \underline{q}$

$$\alpha'^2 = \frac{\alpha^2}{2qk_F}\left\{\int_0^{k_F} k\,dk \int_{-1}^{1} d(\cos\theta)\, PP\frac{1}{\cos\theta + \frac{q}{2k} - \frac{\beta}{k}} - \int_0^{k_F} k'dk' \int_{-1}^{1} d(\cos\theta)\, PP\,\frac{1}{\cos\theta - \frac{q}{2k'} - \frac{\beta}{k'}}\right\} \qquad (\text{IV.iii.1})$$

$$-i\pi\frac{\alpha^2}{2qk_F}\left\{\int_0^{k_F} k\,dk \int_{-1}^{1} d(\cos\theta)\,\delta\left(\cos\theta + \frac{q}{2k} - \frac{\beta}{k}\right) - \int_0^{k_F} k'dk' \int_{-1}^{1} d(\cos\theta)\,\delta\left(\cos\theta - \frac{q}{2k'} - \frac{\beta}{k'}\right)\right\}$$

with $\beta = mu\frac{q_z}{q}$.

We consider first the principal part integrals, show that they give no contribution to first order in the velocity u, and then go on to calculate the contribution from the poles. In the first two terms of (IV.iii.1) the $\cos\theta$ integration is straightforward:

$$\alpha'^{2}_{pp} = \frac{\alpha^2}{2qk_F}\left\{\int_0^{k_F} k\,dk\,\ln\left|\frac{k+q/2-\beta}{k-q/2+\beta}\right| - \int_0^{k_F} k\,dk\,\ln\left|\frac{k-q/2-\beta}{k+q/2+\beta}\right|\right\} \qquad (\text{IV.iii.2})$$

Using the identity (IV.ii.4) we have:

$$\alpha'^{2}_{pp} = \frac{\alpha^2}{2qk_F}\left\{\frac{k_F^2-(q/2-\beta)^2}{2}\ln\left|\frac{k_F+q/2-\beta}{k_F-q/2+\beta}\right| + k_F\left(\frac{q}{2}-\beta\right)\right. \qquad (\text{IV.iii.3})$$

$$\left. -\left[\frac{k_F^2-(q/2+\beta)^2}{2}\ln\left|\frac{k_F-q/2-\beta}{k_F+q/2+\beta}\right| - k_F\left(\frac{q}{2}+\beta\right)\right]\right\}$$

or:

$$\alpha'^{2}_{pp} = \frac{\alpha^2}{2}\left\{1 + \frac{4k_F^2-(q-2\beta)^2}{8qk_F}\ln\left|\frac{2k_F+q-2\beta}{2k_F-q+2\beta}\right| + \frac{4k_F^2-(q+2\beta)^2}{8qk_F}\ln\left|\frac{2k_F+q+2\beta}{2k_F-q-2\beta}\right|\right\} \qquad (\text{IV.iii.4})$$

We note that replacing β by $-\beta$ merely interchanges the two terms in β. As α'^{2}_{pp} is an even function of β we may write:

$$\alpha'^{2}_{pp}(q,\beta) = \alpha'^{2}(q,0) + O(\beta^2) \qquad (\text{IV.iii.5})$$

We note that expression (IV.iii.1) displays two singularities similar to that in the stationary potential. In this expression the two singularities occur at

$$q = 2k_F \pm 2\beta = 2(k_F \pm mu\cos\theta_q) \quad \text{with} \quad \cos\theta_q = q_z/q \qquad (\text{IV.iii.6})$$

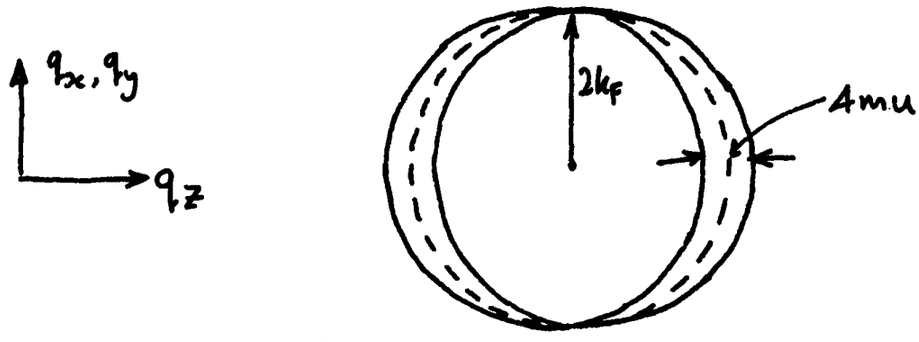


Fig IV.3

Figure IV.3 shows the position of the singularities in q-space. The effect on the phonon spectrum is not clear but there will be a more complex, dynamical, Kohn effect.

We now consider the contribution from the poles of expression (IV.iii.1). The conditions for the poles to exist are:

$$\left.\begin{aligned} \cos\theta + \frac{q}{2k} - \frac{\beta}{k} &= 0 \\ \cos\theta - \frac{q}{2k'} - \frac{\beta}{k'} &= 0 \end{aligned}\right\} \qquad (\text{IV.iii.7})$$

or

$$\left.\begin{aligned} k\cos\theta &= \beta - q/2 \\ k\cos\theta &= \beta + q/2 \end{aligned}\right\}$$

Since k is in the range $0 \leq k \leq k_F$ the condition on $\cos\theta$ may be satisfied if

$$\left.\begin{aligned} k_F &\geq k \geq |\beta - q/2| \\ k_F &\geq k' \geq |\beta + q/2| \end{aligned}\right\} \qquad (\text{IV.iii.8})$$

In both regions k , k' $\leq k_F$ so the condition for either pole to exist is:

$$q \leq 2k_F \pm 2\beta$$

and as the pole itself will only contribute to first order in β the appearance of β in the cut-off is a second order effect. To first order the limit on q is:

$$q \leq 2k_F \qquad (\text{IV.iii.9})$$

The k-integration is then

$$\alpha_p'^2 = -i\pi \frac{\alpha^2}{2qk_F} \left\{ \int_{\beta - q/2}^{k_F} k\,dk - \int_{\beta + q/2}^{k_F} k'\,dk' \right\}$$

$$= -i \frac{\pi}{2} \alpha^2 \frac{\beta}{k_F}$$

$$\alpha_p'^2 = -i \frac{\pi}{2} \alpha^2 \frac{q_z u}{q v_F} \qquad (\text{IV.iii.10})$$

We now add the terms $\alpha_{pp}'^2$ and $\alpha_p'^2$ remembering that α'^2_{pp} has no contribution to first order in the velocity (or β) . From (IV.iii.5) and (IV.iii.10):

$$\alpha'^2(q,\beta) = \alpha'^2(q,0) - i \frac{\pi}{2} \alpha^2 \frac{q_z u}{q v_F} + O(\beta^2)$$

where the second term vanishes for $q > 2k_F$. Inserting this expression in the effective potential (IV.i.9) we obtain:

$$V(q) = \frac{Ze^2}{2\pi^2} \frac{1}{q^2+\alpha^2 - i\alpha^2 \frac{\pi}{2} \frac{q_z u}{q v_F}}$$

For $u \ll v_F$ we may expand this function in a power series in $(q^2 + \alpha^2)$:

$$V(q) = \frac{Ze^2}{2\pi^2} \frac{1}{q^2+\alpha^2} - i \frac{Ze^2}{2\pi^2} \alpha^2 \frac{u}{v_F} \frac{\pi}{2} \frac{q_z}{q} \frac{1}{(q^2+\alpha^2)^2} \qquad (IV.iii.1)$$

In this expression the first term is the screened Coulomb potential we have denoted V_0 . Remembering that this function is now in the moving frame of the ion we have found that to zero order in the velocity the screening cloud moves bodily with the ion. The second term is the velocity dependent V_1 which contains corrections due to the screening and the drift of the electrons. The interesting feature in this expression is its similarity with that obtained by Peierls' Fourier Transform method for weak charge in equation (III.ii.6). In the limit $\tau \to \infty$ for which the factor $\tan^{-1} ql \;/\; (ql - \tan^{-1} ql)$ assumes its asymptotic value $\pi/2ql$ the terms are identical. This surprising result has been discussed at length in chapter III where the $\tau \to \infty$ limit was of interest. We are also interested in the cut-off in q for this may have a more general validity and we apply it to the result of chapter II for the long-range solution in the next chapter.

CHAPTER V

V.i. The Cut-off in the Green's Function Method

In this final chapter we shall give an estimate of the force on the ion. We have derived an expression for the long range behaviour of the distribution function using a Green's Function method in Chapter II. The approximations involved in this calculation prevent us from extrapolating this solution to short range, particularly inside the scattering radius. In Chapters III and IV we looked to other methods for calculating a solution valid in this region. We could not use the spherical harmonic expansion, and discussed a solution by Peierls in the limit of small charge on the ion. In the latter case it was necessary to consider a cut-off in the distribution function and the argument was reinforced by a quantum mechanical analysis. Here the cut-off appeared as the condition for existence of a pole in the dielectric susceptibility of the electron gas. This pole was the sole contribution to the distribution function.

We now return to the long range solution and argue in favour of a cut-off at $r = a$. The quantum mechanical cut-off at $r = a/2$ extrapolates the function beyond the more natural limit and this does in one sense reappear after we have derived the contribution to the force. We find that this force varies as $\xi Z^3 e_c^2$. The factor ξ is even in Z as $\xi \sim (1 + cZ^2)^{-1}$ This force is then identifiable as a screening force. This is not the same as that derived by Peierls in the weak charge approximation; that force, a drift force, does not appear. Furthermore, a simple calculation on Peierls' method shows that there can be no term in the force which is linear in Z . His linear term in the distribution function leads to a quadratic term in the force.

We trace our steps back to the two similar forms of the integral equation written at the end of Chapter II, which enable us to compare the two solutions. We are able to see, by considering the inverse transforms of the source terms in the inhomogeneous equations, that there are two different source terms. In Peierls' case the source varies essentially as $Z e^{-\alpha r}$; this dominates at $r \simeq a$. The Green's Function method yields a source which varies as $Z^2 e^{-r/l}$, and this dominates at $r \simeq l$. This shows that we have found a long range screening correction, and that the Green's Function method has been unable to pick-up the short range drift term.

Continuing along these lines we propose that the distribution function has two terms. The Green's Function term is cut-off at the scattering radius $r = a$, and Peierls' term is cut-off at the quantum mechanical limit $r = a/2$. We return to evaluate the constant ξ from the extra term in

the integral equation and this generates a higher order drift term.

We are then left with a problem; the screening force may be larger than the direct field force. There is at large Z a limiting value to the screening force and this is some consolation. The value is however larger than the direct field force by a factor $1/\alpha$. We are unable to understand this aspect of the result. We propose a further check by considering the total current. However, this leads us towards a reformulation of the Green's Function method taking note of the order of integration. This further calculation is beyond the scope of this thesis. We compare our results with the experimental data as far as this is possible.

V.ii. The Screening Force

We return to the expressions (II.ix.7,9) for the distribution function and its Fourier transform as derived by the Green's Function method.

$$\bar{g}(\underline{k}) = \frac{i}{(2\pi)^3} u \rho_F Q \xi \frac{k_z}{k^2+\alpha^2} \qquad (\overline{V}.ii.1a)$$

$$\bar{f}(\underline{r}) = u \rho_F Q \xi \frac{z}{r} \frac{\partial}{\partial r}\left(\frac{e^{-\alpha r}}{4\pi r}\right) \qquad (\overline{V}.ii.1b)$$

In these expressions Q is the transport cross-section, and ξ is a numerical constant related to integrated functions of $\nu(r) = F(r)/E$ by equation (II.ix.3). In estimating the force we have to make an approximation to the behaviour of the functions inside the scattering region. The

quantum-mechanical argument of Section IV.iii may lead us to propose a cut-off in momentum space at $k = 2k_F$, with $\bar{g}(\underline{k}) = 0$ for $|\underline{k}| > 2k_F$. This corresponds to a cut-off in coordinate space at $r = a/2$. It is tempting to assume the validity of our expression down to this range but we have formally excluded the scattering region itself from our method. We have assumed that the scattered orbits passing through the test point originate only in the backward hemisphere. This limits the range of validity to $r > a$. By that aspect of the model in which all orbits pass through the scattering centre itself the lower limit of the range of validity may be several times the scattering radius.

We evaluate the constant ζ and the force F assuming $f(r)$ has a constant value inside the radius a, equal to its value at that radius. The resulting force is equivalent to that which we would obtain if we used the transformed expression (V.ii.1a) for $k < k_F \simeq 2\pi/a$, and $\bar{g}(\underline{k}) = 0$ for $k > k_F$ We use the results of Section II.ix:

$$\zeta = \frac{1}{1+\epsilon} \qquad (\underline{V}.\text{ii}.2)$$

$$\epsilon = \frac{1}{l}\int_0^\infty dr'\, e^{-r'/l}\, r' \frac{v(r')}{u p_F \zeta} - \frac{\alpha^2}{3}\int_0^\infty dr'\, e^{-r'/l}\left\{\frac{2}{r'^3}\int_0^{r'} dr''\, r''^4 \frac{v(r'')}{u p_F \zeta} - \int_{r'}^\infty dr''\, r'' \frac{v(r'')}{u p_F \zeta}\right\} \qquad (\underline{V}.\text{ii}.3)$$

From equation (V.i.1b)

$$\frac{r' v(r')}{u p_F \xi} = \frac{r'}{z'} \frac{f(r')}{u p_F \xi} = \begin{cases} Q \frac{\partial}{\partial r'} \left(\frac{e^{-\alpha r'}}{4\pi r'} \right) & a < r' < \infty \\ -Q \frac{2}{4\pi a^3 e} & 0 < r' < a \end{cases} \qquad (V.ii.4)$$

We look for the leading order in the parameter l/a and find it to be independent of this parameter. Substituting (V.ii.4) into expression (V.ii,3) we have three terms:

$$\epsilon_1 = -\frac{Q}{4\pi l} \int_0^a dr' e^{-r'/l} r' \frac{2}{a^3 e} + \frac{Q}{4\pi l} \int_a^\infty dr' e^{-r'/l} \frac{\partial}{\partial r'} \left(\frac{e^{-\alpha r'}}{r'} \right)$$

In the first region $e^{-r'/l} \sim 1$ and integrating by parts we see $\epsilon_1 \sim O(a/l)$.

$$\epsilon_{2\, r<a} = \frac{\alpha^2 Q}{12\pi} \int_0^a dr' e^{-r'/l} \left\{ \frac{2}{r'^3} \int_0^{r'} dr'' r''^4 \frac{2}{a^3 e} - \int_{r'}^a dr'' r'' \frac{2}{a^3 e} - \int_a^\infty dr'' \frac{d}{dr''} \left(\frac{e^{-\alpha r''}}{r''} \right) \right\}$$

Once more, in this region, $e^{-r'/l} \sim 1$ and $\epsilon_2 = \frac{\alpha^2 Q}{20\pi e}$
Similarly in ϵ_3 we find the leading order to be constant if we replace $e^{-r'/l}$ by 1. Then:

$$\epsilon_{3\, r'>a} = \frac{\alpha^2 Q}{12\pi} \int_a^\infty dr' e^{-r'/l} \left\{ \frac{2}{r'^3} \int_0^a dr'' r''^4 \frac{2}{a^3 e} - \frac{2}{r'^3} \int_a^{r'} dr'' r''^3 \frac{d}{dr''} \left(\frac{e^{-\alpha r''}}{r''} \right) + \int_{r'}^\infty dr'' \frac{d}{dr''} \left(\frac{e^{-\alpha r''}}{r''} \right) \right\}$$

$$= \frac{\alpha^2 Q}{12\pi} \int_a^\infty dr' e^{-r'/l} \left\{ 14\tfrac{4}{5} \frac{a^2}{e r'^3} - 6a^2 \frac{e^{-\alpha r'}}{r'^3} - 6a \frac{e^{-\alpha r'}}{r'^2} - 3 \frac{e^{-\alpha r'}}{r'} \right\}$$

$$= \frac{\alpha^2 Q}{12\pi} \frac{7}{5e} + O\left(\frac{a}{l}\right)$$

Adding terms:

$$\epsilon = \epsilon_1 + \epsilon_2 + \epsilon_3 = \frac{\alpha^2 Q}{6\pi e} + O\left(\frac{a}{l}\right)$$

Then

$$\zeta = \frac{1}{1 + \frac{\alpha^2 Q}{6\pi e}} \qquad (\bar{V}.ii.5)$$

and we obtain the force using expression (V.ii.4) for the function $r\nu(r)$ and expression (IIi.19):

$$F = -Z u p_F Q \zeta \frac{\alpha^2}{12\pi} \left\{ \int_0^a dr \, \frac{2r}{a^3 e} - \int_a^\infty dr \, \frac{d}{dr}\left(\frac{e^{-\alpha r}}{r}\right) \right\}$$

$$= -Z \frac{u p_F}{a} \zeta \frac{\alpha^2 Q}{6\pi e}$$

Throughout this analysis we have considered a phenomenological ion velocity u which is related to the velocity u_0 of the ion in the lattice by the drift velocity u_E as in expression (II.i.14)

$$u = u_0 - \frac{e_c \tau E}{m}$$

Then in the case of a stationary ion, $u_0 = 0$, and

$$F = Z e_c E \frac{l}{a} \frac{\frac{\alpha^2 Q}{6\pi e}}{1 + \frac{\alpha^2 Q}{6\pi e}} \qquad (\bar{V}.ii.6)$$

From the discussion in the introductory Section I.i. we may be able to consider this term as a screening force. From its definition (II.i.15) α^2 varies as $(-ee_c)$. The transport cross-section Q varies as $(Zee_c)^2$. The force is

then odd in Z and even in e_c , with negative sign for $e_c \alpha^2 \propto -|e|^3$. This is the behaviour we would expect from a screening force, and we write this with the direct force:

$$F = ZeE \left[1 - \frac{l}{a} \frac{\frac{\alpha^2 Q}{6\pi e}}{1 + \frac{\alpha^2 Q}{6\pi e}} \right] \qquad (\underline{V}.ii.7)$$

We are now able to see a problem in this interpretation. The problem, which we shall not be able to resolve, is the possible dominance of this force at large Z . It does converge to the value l/a , but we have made no restriction on this numerical factor in our analysis. The problem may be connected with the choice of cut-off but this does not look promising because a larger cut-off need only be several times the screening radius and not in any way related to the mean freepath l .

The problem may also be related to the approximations of the model. The analysis is not sensitive to the behaviour inside the screening radius and we shall see this already in the next section. On the other hand we were able to obtain sensible results in the quantum mechanical analysis if we ignored the effect of the mean freepath of the electrons at short range. Indeed we used this to explain the failure of the spherical harmonics expansion. But the possibility of the distribution function changing sign in this region has not been fully investigated and there may be an alternative physical explanation to this term. We shall finally suggest that by looking for the total current we may obtain more information on this problem. We shall now turn to Peierls'

force and see how we have already missed a term in the distribution function which is dominating at short range.

V.iii The Drift Force

We now return to the force derived by Peierls:

$$F_P = -Z^2 e_c E \frac{1}{12\pi} \frac{l}{a} \qquad \text{(from AII.25)}$$

Since this term is even in the ionic charge Z and odd in the carrier charge e_c, we may identify it as a drift force. As such we can see that it bears no resemblance to the screening force of the previous section and we now look at this term again. We first of all show from the general solution to g_1, at small Z there can be no linear term in the force. We do this by considering the alternative force in terms of the function ϕ, using the argument of Section II.i to maintain the correct order of integration. The force Peierls finally calculates is quadratic, and the Green's Function term is only linear at large Z. We return to the integral equations for the two distribution functions, find that the equivalent homogeneous equations are identical and consider the inverse transforms of the inhomogeneous terms. These transforms show that the Green's Function term is a long-range effect, varying as $e^{-r/\lambda}$ and Peierls' weak charge term is essentially short-range, varying as e^{-ar}. The short-range term has been missed in the Green's Function method by its approximations.

We then propose to add the two source terms into the integral equation and once more evaluate the constant β.

This does not affect the screening force already calculated but adds further drift force in addition to that calculated by Peierls.

We now return to the second formulation of the force given in Section II.i as from equation (II.i.23)

$$F = -\frac{\alpha^2}{4\pi e^2 m p_F \tau} \int d^3\underline{r}\, d^3\underline{p}\; p_z \varphi$$

We remember the discussion of that section regarding the order of integration, i.e. we integrate over a sausage with $z \gg x,y$ and then let $r \to \infty$. We also identify φ with the transform of the function g_1, of Peierls' calculation for:

$$g_1 = g_\infty - g_0 = g - u p_z \delta(k)$$

and from equation (II.i.22) $\varphi = f - u p_z$

From this we can see that

$$\int \varphi(r)\, d^3\underline{r} = g_1(k)\Big|_{k\to 0} \qquad (\underline{V}.iii.1)$$

We take care in proceeding to this limit. The integration in coordinate space may be effected by including a factor:

$$e^{-\beta z^2/2 - \gamma(x^2+y^2)/2}$$

with $\beta \ll \gamma$. In momentum space this factor is equivalent to

$$e^{-k_z^2/2\beta - (k_x^2 + k_y^2)/2\gamma}$$

which corresponds to the limit $k \to 0$ with $k_z \ll k$. We now show that in this limit Peierls' expression for g_1 leads to a zero force.

From Appendix II this expression may be written:

$$g_1 = -\frac{\alpha^2}{k^2}\bar{g}_1 + \frac{\frac{1}{\tau}\left(1+\frac{\alpha^2}{k^2}\right)\bar{g}_1}{\frac{i}{m}(\underline{p}.\underline{k})+\frac{1}{\tau}} + \frac{\frac{iuk_z}{2\pi^2}\frac{Ze^2}{\alpha^2+k^2}}{\frac{i}{m}(\underline{p}.\underline{k})+\frac{1}{\tau}} \qquad (\overline{V}.iii.2)$$

Using an identity similar to (II.vi.8) we have:

$$\int d^3\underline{p}\; p_z g_1 = \int d^3\underline{p}\left[\frac{k_z}{k^2}(\underline{p}.\underline{k})g_1 + \text{terms} \perp k_z\right]$$

On integration the second term vanishes for all the terms in g_1. Of the remaining three terms the first is trivial:

$$\int d^3\underline{p}\;(\underline{p}.\underline{k}) = 0$$

The second is:

$$\int d^3\underline{p}\;\frac{(\underline{p}.\underline{k})}{\frac{i}{m}(\underline{p}.\underline{k})+\frac{1}{\tau}}\;\frac{k_z}{k^2}\frac{1}{\tau}\left(1+\frac{\alpha^2}{k^2}\right)\bar{g}_1$$

We choose $\underline{k}$ to be the z-axis of the $\underline{p}$ integration.

$$\int p^2 dp\; 2\pi \int_{-1}^{1} d(\cos\theta)\left(\frac{\cos\theta}{\cos\theta - \frac{im}{\tau pk}}\right)\left(-\frac{im}{\tau}\right)\left(1+\frac{\alpha^2}{k^2}\right)\frac{k_z}{k^2}\bar{g}_1$$

With the factor $\frac{\partial n_0}{\partial p}$ understood, the integrations are straightforward:

$$-4\pi\,\frac{im}{\tau}\,p_F^2\left[1-\frac{\tan^{-1}kl}{kl}\right]\left(1+\frac{\alpha^2}{k^2}\right)\frac{k_z}{k^2}\bar{g}_1$$

As $k \to 0$, $\bar{g}_1$ varies as k_z and this term varies as

$$\left[1 - \frac{\tan^{-1} kl}{kl}\right] \left(\frac{k^2+\alpha^2}{k^2}\right) \frac{k_z}{k^2} k_z \longrightarrow \frac{k_z^2}{k^2} \qquad (\bar{V}.iii.3)$$

which vanishes in the limit if $k_z \ll k$. The third term may be similarly shown to vary as k_z^2 as $k \to 0$ and so too will vanish in the limit.

We appear to have shown that there can be no force at all due to the motion of the ion. But in using the function g_1 instead of ϕ we are strictly only considering the first order term and that at small Z. So our correction of $Z^3/(1+cZ^2)$ will not appear, neither will Peierls' term of order Z^2. By using the expression $Z\frac{\partial v_1}{\partial r}$ with the average function $\bar{g}_1$ he has generated a higher order term in the force.

We have satisfied ourselves that the screening force, in first order at large Z, does not contradict Peierls' result at small Z. We now try to understand how it is that Peierls' term has been missed in the Green's Function method. To do this we return to the Fourier transforms of the integral equations for $\bar{g}$ from the two methods. These are written together in Chapter II, equations (II.ix.5 and 6). We noticed at that stage that the equivalent homogeneous equations are identical; we now look at the weak charge calculation in a Green's Function formalism in order to understand the similarity.

In Peierls' calculation the zero order term f_0 is shown to be up_z/τ and the equation for the first order term f_1 of the distribution function may be written:

$$D f_1 - V_0 f_0 + S_0 f_1 - S_i f_1 = \frac{\partial V_1}{\partial \underline{r}} \cdot \underline{p} \qquad (\underline{V}.iii.4)$$

The operators D and V_0 are the diffusion and potential terms in the absence of the velocity u. S_i and S_0 are the scattering in and scattering out terms. We may then identify the Green's Function:

$$\frac{1}{D + S_0} = \frac{1}{\frac{i}{m}(\underline{p}.\underline{k}) + \frac{1}{\tau}} \qquad (\underline{V}.iii.5)$$

Then $$f_1 = \frac{1}{D + S_0} \left\{ V_0 f_0 + \frac{\partial V_1}{\partial \underline{r}} \cdot \underline{p} + S_i f_1 \right\} \qquad (\underline{V}.iii.6)$$

In Chapter II we have not ordered the terms in Z and the equation for f is still:

$$(D - V_0 + S_0) f = \frac{u p_z}{\tau} + \frac{\partial V_1}{\partial \underline{r}} \cdot \underline{p} + S_i f = S$$

We constructed the Green's Function

$$G(\underline{r}, \underline{p} \,|\, \underline{r}', \underline{p}') = \frac{1}{D - V_0 + S_0} \qquad (\underline{V}.iii.7)$$

to write the solution for f:

$$f = \frac{1}{D - V_0 + S_0} S \qquad (\underline{V}.iii.8)$$

The similarity of the two methods is made apparent if we now consider Z to be small and expand the second Greens Function in V_0:

$$f = \frac{1}{D+S_0} S + \frac{1}{D+S_0} V \frac{1}{D+S_0} S \qquad (\underline{V}.iii.9)$$

The first term then represents the homogeneous term in the integral equation and we can see that with the Green's Function essentially the same these terms arise in a similar way in both methods. The second term only arises in the weak charge limit and we can see how we may generate Peierls' inhomogeneous term when we take that limit of our more general case. We can in particular identify V_0 in the numerator of the final term of equation (II.ix.6)

We did not take this weak charge limit in our calculations but rather made a long-range calculation. In doing this we appear to have lost this final term altogether. We obtain a clue to this by comparing the inverse transforms of the inhomogeneous terms in each of the equations (II.ix 5 and 6). We have already derived this expression in the case of equation 5. We have:

$$T\left[-i\frac{u\rho_F Q}{2\pi^2}\int\frac{k_z}{k^2}\left(\frac{\tan^{-1}kl}{kl}-1\right)\right] = u\rho_F Q\int\frac{z}{r}\frac{e^{-r/l}}{4\pi r^2} \qquad (\underline{V}.iii.10)$$

The inverse transform of Peierls'term may be shown to be:

$$T\left[i\frac{uml}{2\pi^2\rho_F}\frac{Ze^2}{k^2+\alpha^2}k_z\frac{\tan^{-1}kl}{kl}\right]$$

$$=-\frac{u}{2v_F}\frac{Ze^2}{\alpha}\frac{z}{r}\frac{\partial}{\partial r}\frac{1}{r}\left\{\frac{2}{\alpha l}e^{-\alpha r}-e^{\alpha r}Ei\left[-\left(\frac{1}{l}+\alpha\right)r\right]+e^{-\alpha r}\overline{Ei}\left[\left(\alpha-\frac{1}{l}\right)r\right]\right\} \qquad (\underline{V}.iii.11)$$

The second and third terms may be written:

$$e^{-r/l}\left\{e^{-(\alpha-\frac{1}{l})r}\overline{Ei}\left[(\alpha-\tfrac{1}{l})r\right]-e^{-(\alpha+\frac{1}{l})r}Ei\left[-(\alpha+\tfrac{1}{l})r\right]\right\}$$

Since $e^{-x}\bar{E}i(x)$ and $e^{x}Ei(-x)$ are both ~ 1 at large arguments this expression is essentially varying as $e^{-\alpha r}$. By comparing this with the $e^{-r/l}$ behaviour of the previous term we can understand their different yet complimentary nature. In ignoring the behaviour near the scattering radius the Green's Function method has lost Peierls' short-range drift term. We have already shown a long-range screening term; we now add the inhomogeneous sources in the integral equation and show that this will give us a second drift force.

Since the integral equations are linear we may add the solutions to give:

$$\nu = \nu_{G.F.} + \nu_{P.} \qquad (\bar{V}.iii.12)$$

These will yield the screening force already calculated, and the drift force of Peierls. But the constant ξ which was related to integrated functions of ν will now contain another term. Following the prescription of Chapter II:

$$\xi = 1 - \xi\epsilon + \eta \qquad (\bar{V}.iii.13)$$

where η is a term similar to ϵ having the form

$$u_F^2\eta = \frac{1}{l}\int_0^\infty dr'\, e^{-r'/l}\, r'\nu_p(r') - \frac{\alpha^2}{3}\int_0^\infty dr'\, e^{-r'/l}\left\{\frac{2}{r'^3}\int_0^{r'} dr''\, r''^4\nu_p(r'') - \int_{r'}^\infty dr''\, r''\nu_p(r'')\right\}$$

Then $$\xi = \frac{1+\eta}{1+\epsilon} \qquad (\bar{V}.iii.14)$$

The term $\frac{1}{1+\epsilon}$ yields the same screening force as before, but since η is linear in Z the second term, $\eta/(1+\epsilon)$ will give

another drift force. The factor η is given approximately by $\alpha^2 Q / 15eZ$, and the total force is then:

$$F = ZeE\left[1 - \frac{l}{a}\frac{\frac{\alpha^2 Q}{6\pi e}}{1+\frac{\alpha^2 Q}{6\pi e}}\right] - Z^2 eE\frac{l}{a}\left[\frac{1}{12\pi} + \frac{\frac{\alpha^2 Q}{6\pi e}}{1+\frac{\alpha^2 Q}{6\pi e}}\frac{\alpha^2 Q}{15eZ^2}\right] \qquad (\bar{V}.iii.15)$$

The ratio of mean freepath to screening radius l/a is in most metals large enough to account for the large values of effective charge discussed in the experimental survey of Section I.ii. However, the problems over interpretations suggest that we are not yet able to make a comparison with any particular experiment.

We have not been able to resolve the question of the behaviour of the distribution function at short range. The present Green's Function method has already missed a drift term, and both solutions may be concealing a change in sign inside the screening radius. The final expression for the forces has its main contribution from radii in the region of the screening radius. We leave the problem by suggesting a further calculation of the current for this may not rely on the short range behaviour of the distribution function. The velocity dependent term $\delta\underline{j}$ of the current density $\underline{j}$ is related to the function φ of Chapter II by:

$$\underline{j} = -n_0 e\underline{u} + \delta\underline{j} \qquad (\bar{V}.iii.16)$$

$$\delta\underline{j} = \delta j_z = -\frac{e}{m}\int p_z \varphi\, d^3p \qquad (\bar{V}.iii.17)$$

The total current associated with the motion of the ion is:

$$\delta I = -\frac{e}{m}\iint p_z \varphi \, d^3\underline{r} \, d^3\underline{p} \qquad (\bar{V}.iii.18)$$

Apart from factors this is the same expression as (II.i. 24) for the force. We expect then that the argument concerning the order of integration will apply here too. This expression will not necessarily yield the same result as we have obtained in this thesis for our approximations may have different effects in the integrals.

Furthermore, the previous expression for the force may have assumed a trivial relationship between the force and the current which in this case does not exist. We should have to compute this expression by integrating in the way discussed in Chapter II. However, we have had to construct an elaborate formalism already and it may not be easily adapted for a change in the order of integration.

APPENDIX I

A.I.a The Boltzmann Equation in the Frame of the Ion

The following analysis has been given by A.K. Das in his thesis. The general form of the Boltzmann Equation is:

$$\frac{\partial n}{\partial t} = \underline{v}.\nabla_r n - \underline{F}.\nabla_p n + \int W(\underline{P}', \underline{P})\, n(\underline{P}', \underline{r})\, d^3\underline{P}' - \int W(\underline{P}, \underline{P}')\, n(\underline{P}, \underline{r})\, d^3\underline{P}' \qquad \text{(AI.1)}$$

For isotropic elastic scattering the transition probability W contains a factor $\delta(E'-E)$ and if Θ is the scattering angle we may write

$$W(\underline{P}',\underline{P}) = \frac{1}{4\pi} Y(\Theta)\,\delta(E'-E) \qquad (AI.2)$$

The scattering terms are then written:

$$-\frac{1}{4\pi}\int Y(\Theta)\, n(\underline{P})\, d\omega_{\underline{P}'} + \frac{1}{4\pi}\int Y(\Theta)\, n(\underline{P}')\, d\omega_{\underline{P}'} \qquad (AI.3)$$

We now use the concept of a "collision time" (Peierls 1955) which is defined by

$$\frac{1}{\tau} = \frac{1}{4\pi}\int Y(\Theta)\, d\omega_{\underline{P}'} \qquad (AI.4)$$

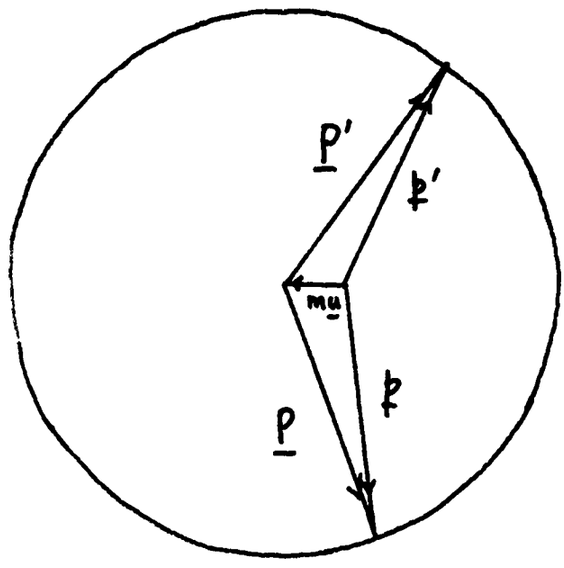
Then

$$\bar{n} = \frac{1}{4\pi}\int n(\underline{P}')\, d\omega_{\underline{P}'} = \frac{\int Y(\Theta)\, n(P')\, d\omega_{P'}}{\int Y(\Theta)\, d\omega_{P'}} = \frac{\tau}{4\pi}\int Y(\Theta) n(P')\, d\omega_{P'}$$

to give

$$-\frac{n}{\tau} + \frac{1}{4\pi\tau}\int n(\underline{P}')\, d\omega_{\underline{P}'} \qquad (AI.5)$$

We wish to transform the second of these terms into the moving frame of the ion.



$$|\underline{P}| = |\underline{P}'|$$

The transformation is defined by:

$$\underline{p}' = m\underline{u} + \underline{P}' \qquad \text{(AI.6)}$$

We can see from the diagram that the magnitude of any momentum vector in the stationary frame is constant, and by defining a unit vector in the direction of $\underline{P}'$ we may write

$$\underline{p}' = m\underline{u} + \underline{a}\,|\underline{p} - m\underline{u}| \qquad \text{(AI.7)}$$

Then all $\underline{p}'$ vectors are generated if we let $\underline{a}$ be a unit vector in an arbitrary direction. Neglecting the term in u^2 we write

$$|\underline{p} - m\underline{u}| = p^2 - 2m\,\underline{u}.\underline{p}$$

and

$$|\underline{p} - m\underline{u}| = p - m\,\frac{\underline{u}.\underline{p}}{p} \qquad \text{(AI.8)}$$

The integr' we seek is then:

$$\int n(\underline{p}')\, d\omega_{\underline{p}'} = \int n\left[m\underline{u} + \underline{a}\left(p - m\,\frac{\underline{u}\cdot\underline{p}}{p}\right)\right] d\Omega_a \qquad \text{(AI.9)}$$

Since $\underline{a}$ is arbitrary we may write $\underline{a}\,p = \underline{p}'$ and then

$$\int n(\underline{p}')\, d\omega_{\underline{p}'} = \int n\left[\underline{p}' + m\underline{u} - m\,\frac{\underline{u}\cdot\underline{p}}{p^2}\,\underline{p}'\right] d\Omega_{\underline{p}'}$$

We expand the integrand in a Taylor' series to first order in u :

$$\int d\Omega_{\underline{p}'}\left\{ n(\underline{p}') + m\left(\underline{u} - \frac{\underline{u}\cdot\underline{p}}{p^2}\,\underline{p}'\right)\frac{\partial n(\underline{p}')}{\partial \underline{p}'}\right\} \qquad \text{(AI.10)}$$

We now write $n = n_0 + n_1$, and consider terms to first order, and note that since n_0 is isotropic

$$\frac{\partial n_0}{\partial \underline{p}'} = 2\underline{p}'\,\frac{\partial n_0}{\partial p'^2}$$

Since $$p'^2 = p^2$$

$$\frac{\partial n_0}{\partial p'^2} = \frac{1}{2p}\,\frac{\partial n_0}{\partial p}$$

Then

$$I = 4\pi(\bar{n}_0 + \bar{n}_1) + \int \frac{m}{p}(\underline{u}\cdot\underline{p}' - \underline{u}\cdot\underline{p})\cdot\frac{\partial n_0}{\partial p}\, d\Omega_{p'} \qquad (AI.11)$$

$$= 4\pi\bar{n}_1 + \frac{m}{p}(\underline{u}\cdot\underline{p})\frac{\partial n_0}{\partial p}\, 4\pi$$

So

$$\frac{1}{4\pi\tau}\int n(\underline{p}')\, d\omega_{\underline{p}'} = \frac{\bar{n}_1}{\tau} + \frac{mu}{\tau}\frac{p_z}{p}\frac{\partial n_0}{\partial p} \qquad (AI.12)$$

The Boltzmann Equation is then:

$$\frac{\partial n}{\partial t} = \underline{v}\cdot\nabla_r(n_0+n_1) - \underline{F}\cdot\nabla_p(n_0+n_1) - \frac{n_0+n_1}{\tau} + \frac{\bar{n}_1}{\tau} + \frac{mu}{\tau}\frac{p_z}{p}\frac{\partial n_0}{\partial p}$$

$$\underline{F} = \frac{\partial V_0}{\partial \underline{r}} + \frac{\partial V_1}{\partial \underline{r}}$$

The equation to first order is then

$$\frac{\underline{p}}{m}\cdot\frac{\partial n_1}{\partial \underline{r}} - \frac{\partial V_0}{\partial \underline{r}}\cdot\frac{\partial n_1}{\partial \underline{p}} - \frac{\partial V_1}{\partial \underline{r}}\cdot\frac{\partial n_0}{\partial \underline{p}} + \frac{1}{\tau}(\bar{n}_1 - n_1) = -\frac{mu}{\tau}\frac{p_z}{p}\frac{\partial n_0}{\partial p} \qquad (AI.13)$$

A.1.b. The Spherical Harmonics Expansion using a Variational Method

We do not simply introduce the harmonic expansion into the Boltzmann and solve the equations so obtained for the coefficients in the expansion. There is a difficulty here in how we could terminate the series. We are able to answer this problem to some extent by using a variational technique. The Boltzmann equation is considered as an Enler variational equation to some integral I. We then introduce the harmonic expansion into this function and obtain a set of equations in the harmonics by finding the Enler variational equation for each of the coefficients. The truncation of the series is now made clear, for we may consider only those equations obtained by variation with respect to the retained coefficients.

In this appendix we shall discuss the variational method and the harmonic expansion and obtain the equations in the first two harmonics.

In order to obtain the Boltzmann equation as a variational equation we have to construct an integral which is quadratic in the distribution function n_1 . This method has been discussed in Ziman (1969) and in essence requires an orthogonal function $\tilde{n}_1$. That this is so is easily learnt if we try the function n_1, itself. For example:

$$\delta \int n_1(\underline{r},\underline{p})\, \underline{v} \cdot \frac{\partial n_1}{\partial \underline{r}}\, d^3\underline{r}\, d^3\underline{p} = \delta n_1 \left\{ \underline{v} \cdot \frac{\partial n_1}{\partial \underline{r}} - \frac{\partial}{\partial \underline{r}} (\underline{v} n_1) \right\} \qquad \text{(AI.14)}$$

This function is trivially zero. The simplest form of orthogonal function is $n_1(r,-p)$ and this is the form Das takes. The first term in the Boltzmann equation then appears in the following way:

$$I_1 = \frac{1}{2}\iint d^3r\, d^3p\; n_1(r,-p)\, v \cdot \frac{\partial n_1(r,p)}{\partial r} \qquad \text{(AI.15)}$$

So

$$\delta I_1 = \frac{1}{2}\iint d^3r\, d^3p \left\{ \delta n_1(r,-p)\, v \cdot \frac{\partial n_1(r,p)}{\partial r} + n_1(r,-p)\, v \cdot \frac{\partial}{\partial r}\delta n_1(r,p) \right\}$$

We integrate the second term by parts to give

$$\frac{1}{2}\left[\int d^3p\; n_1(r,-p)\, v\, \delta n_1(r,p)\right]_S - \frac{1}{2}\iint d^3r\, d^3p\; \frac{\partial n_1(r,-p)}{\partial r}\, v\, \delta n_1(r,p)$$

If we let the surface S extend to infinity the first term does not contribute. In the second term we may change the sign of the momentum to give

$$\delta I_1 = \iint d^3r\, d^3p\; \delta n_1(r,-p)\, v \cdot \frac{\partial n_1}{\partial r} \qquad \text{(AI.16)}$$

where both terms are the same. The variation of I_1 with respect to $n_1(r,-p)$ then gives the first term in the Boltzmann equation. A similar argument shows that three of the terms are given by:

$$\frac{1}{2}\iint d^3r\, d^3p\; n_1(r,-p)\left[v \cdot \frac{\partial n_1}{\partial r} - \frac{\partial V_0}{\partial r} \cdot \frac{\partial n_1}{\partial p} + \frac{n_1}{\tau}\right] \qquad \text{(AI.17)}$$

and the source terms are given by:

$$\iint d^3\underline{r}\, d^3\underline{p} \left\{ -\eta_1(\underline{r},-\underline{p}) \frac{\partial V}{\partial \underline{r}} \cdot \frac{\partial n_0}{\partial \underline{p}} - \frac{1}{8\pi\tau} \int n_1(\underline{r},-\underline{p}') \eta_1(r,p) d\Omega_{p'} + \frac{mu}{\tau} n_1(\underline{r},-\underline{p}) \frac{\partial n_0}{\partial p} \frac{p_z}{p} \right\} \tag{AI.18}$$

We now expand both of the distribution functions in special harmonics in the following way:

$$\eta_1(\underline{r}, \pm\underline{p}) = \eta^{\pm} = \pm \sum_{l=0} \sum_{m} C(l,m) \varphi_l(r,p)\ Y_l^m(\hat{\underline{r}})\, Y_{l+1}^{m*}(\hat{\underline{p}}) + \sum_{l=1} \sum_{m} C(l,m) \psi_l(r,p)\, Y_l^m(\hat{\underline{r}})\, Y_{l-1}^{m*}(\hat{\underline{p}}) \tag{AI.19}$$

The constants $C(l,m)$ are related to the Clebsch-Gordon coefficients and arise from the normalisation of the spherical harmonics Y_l^m. The first two terms in the expansion are:

$$\eta^{\pm} = \sqrt{\frac{1}{4\pi}} \left(Y_1^0(\hat{\underline{r}})\, \psi_1 \pm Y_1^0(\hat{\underline{p}})\, \varphi_0 \right) \tag{AI.20}$$

The evaluation of the variational integral with this form of the distribution function is a straightforward, even if lengthy, calculation. It is simplified by using the following identities:

$$i\ \underline{p} \cdot \frac{\partial}{\partial \underline{r}} Y_1^0(\hat{\underline{r}}) = \underline{p} \cdot \nabla\left(c\frac{\underline{r}}{r}\right) = -\frac{\underline{p}\cdot\underline{r}}{r^2} Y_1^0(\hat{\underline{r}}) + \frac{p}{r} Y_1^0(\hat{\underline{p}}) \tag{AI.21}$$

ii

$$\iint Y_1^0(\hat{\underline{r}})\, Y_1^0(\hat{\underline{p}})\, d\omega_r\, d\omega_p = 0 \qquad \text{(AI.22)}$$

iii

$$\iint Y_1^0(\hat{\underline{r}})\, Y_1^0(\hat{\underline{r}})\, d\omega_r\, d\omega_p = 4\pi \qquad \text{(AI.23)}$$

iv

$$\iint Y_1^0(\hat{\underline{r}})\, Y_1^0(\hat{\underline{r}})\, (\underline{r}\cdot\underline{p})\, d\omega_r\, d\omega_p = 0 \qquad \text{(AI.24)}$$

v

$$\iint Y_1^0(\hat{\underline{r}})\, Y_1^0(\hat{\underline{p}})\, (\underline{p}\cdot\underline{r})\, d\omega_r\, d\omega_p = \frac{4\pi}{3} pr \qquad \text{(AI.25)}$$

The integral may then be shown to be:

$$\iint r^2 dr\, p^2 dp \left\{ \frac{p}{6m}\left(\psi_1 \frac{\partial \phi_0}{\partial r} - \phi_0 \frac{\partial \psi_1}{\partial r}\right) - \frac{\partial V_0}{\partial r}\left(\psi_1 \frac{\partial \phi_0}{\partial p} - \phi_0 \frac{\partial \psi_1}{\partial p}\right) - \left(\frac{p}{3m\tau} + \frac{1}{3p}\frac{\partial V_0}{\partial r}\right)\phi_0 \psi_1 \right.$$

$$\left. + \frac{4\pi}{3\sqrt{3}}\left(\frac{\partial \chi}{\partial r} + \frac{2\chi}{r}\right)\phi_0 - \frac{1}{2\tau}\phi_0^2 - \frac{mu}{\tau}\frac{4\pi}{\sqrt{3}}\frac{\partial n_0}{\partial p}\phi_0 \right\} \qquad \text{(AI.26)}$$

The variation with respect to ψ_1 then gives:

$$\frac{\delta I}{\delta \psi_1} = 0$$

$$\frac{r^2 p^3}{3m}\frac{\partial \phi_0}{\partial r} - \frac{r^2 p^2}{3}\frac{\partial V_0}{\partial r}\frac{\partial \phi_0}{\partial p} - \frac{2}{3} r^2 p \frac{\partial V_0}{\partial r}\phi_0 = 0 \qquad \text{(AI.27)}$$

and the variation with respect to φ_0 gives:

$$\frac{\delta I}{\delta \varphi_0} = 0$$

$$-\frac{r^2 p^3}{3m}\frac{\partial \psi_1}{\partial r} - \frac{2}{3}\frac{r p^3}{m}\psi_1 + \frac{r^2 p^2}{3}\frac{\partial V_0}{\partial r}\frac{\partial \psi_1}{\partial p} + r^2 p^2 \frac{4\pi}{3\sqrt{3}}\left(\frac{\partial \chi}{\partial r} + \frac{2\chi}{r}\right) \qquad (AI.28)$$

$$-\frac{r^2 p^2}{\tau}\varphi_0 - \frac{mu}{\tau}\frac{4\pi}{\sqrt{3}} r^2 p^2 \frac{\partial n_0}{\partial p} = 0$$

In a private communication Das has also calculated the four equations in the first four coefficients:

From

$$\frac{\delta I'}{\delta \varphi_0} = 0$$

$$\frac{p}{3mr^2}\frac{\partial}{\partial r}(r^2\psi_1) - \frac{\sqrt{5}}{3}\frac{p}{3mr^2}\frac{\partial}{\partial r}(r^2\varphi_1) + \frac{\varphi_0}{\tau} \qquad (AI.29)$$

$$= \frac{4\pi}{3\sqrt{3}}\frac{\partial n_0}{\partial p}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\chi) - \frac{4\pi}{\sqrt{3}}\frac{m^2 u}{\tau}\frac{1}{p}\left(\frac{\partial^2 n_0}{\partial p^2} - \frac{1}{p}\frac{\partial n_0}{\partial p}\right)V_0$$

From

$$\frac{\delta I'}{\delta \psi_1} = 0$$

$$\frac{p}{3m}\frac{\partial \varphi_0}{\partial r} + \frac{\sqrt{5}}{3}\frac{p}{m}\frac{1}{r^3}\frac{\partial}{\partial r}(r^3\psi_2) = -\frac{4\pi}{3\sqrt{3}} mu\left(\frac{2}{p}\frac{\partial n_0}{\partial p} + \frac{\partial^2 n_0}{\partial p^2}\right)\frac{\partial V_0}{\partial r} \qquad (AI.30)$$

From $$\frac{\delta I'}{\delta \Phi_1} = 0$$

$$\frac{\sqrt{5}}{3}\frac{p}{m}\frac{\partial \Phi_0}{\partial r} + \frac{1}{6}\frac{p}{mr^3}\frac{\partial}{\partial r}(r^3\Psi_2) - \frac{5}{2}\frac{\Phi_1}{\tau} = -\frac{\sqrt{5}}{3}\frac{4\pi}{\sqrt{3}}mu\left(\frac{\partial^2 n_0}{\partial p^2} - \frac{1}{p}\frac{\partial n_0}{\partial p}\right)\frac{\partial V_0}{\partial r} \qquad \text{(AI.31)}$$

From $$\frac{\delta I'}{\delta \Psi_2} = 0$$

$$-\frac{1}{6}\frac{p}{m}r\frac{\partial}{\partial r}\left(\frac{\Phi_1}{r}\right) - \frac{\sqrt{5}}{3}\frac{p}{m}r\frac{\partial}{\partial r}\left(\frac{\Psi_1}{r}\right) + \frac{5}{2}\frac{\Psi_2}{\tau} = -\frac{\sqrt{5}}{3}\frac{4\pi}{\sqrt{3}}\frac{\partial n_0}{\partial p}r\frac{\partial}{\partial r}\left(\frac{\chi_1}{r}\right) \qquad \text{(AI.32)}$$

APPENDIX II

Peierls' Fourier Transform method for weak charge

The Boltzmann equation for electrons in free space, in the presence of a uniform positive charge density ("jellium") and of a positive ion of charge Ze, moving in the z direction with velocity u, has the form:

$$\frac{1}{m} p \frac{\partial n_1}{\partial z} - \frac{\partial V_0}{\partial z} \cdot \frac{\partial n_1}{\partial p} - \frac{\partial V_1}{\partial z} \cdot \frac{\partial n_0}{\partial p} + \frac{1}{\tau}(n_1 - \bar{n}_1) = - \frac{u}{v} p_z \frac{\partial n_0}{\partial E} \qquad (A\,II.1)$$

Here terms of higher than the first order in u have been neglected, n_1 is the first-order deviation of the electron density in phase space from the equilibrium distribution n_0, V_0 is e times the potential due to an ion at rest in the electron gas (which satisfies the Thomas-Fermi equation), V_1 is the first-order correction due to the motion. τ is the collision time, assumed constant, and $\bar{n}_1$ is the average of n_1 over all directions

of the momentum, $\underline{p}$. The equation applies in the co-moving coordinate system in which the ion is at rest.

Now let $$n_1 = f(r, p) \frac{\partial n_0}{\partial E} \qquad \text{(AII.2)}$$

where E is understood to be

$$E = \frac{1}{2m} p^2 + V_0(r) \qquad \text{(AII.3)}$$

Then (1) becomes:

$$\frac{1}{m} p \cdot \frac{\partial f}{\partial r} - \frac{\partial V_0}{\partial r} \cdot \frac{\partial f}{\partial p} - \frac{1}{m} \frac{\partial V_1}{\partial r} \cdot p + \frac{1}{\tau}(f - \bar{f}) = -\frac{u}{\tau} p_z \qquad \text{(AII.4)}$$

This is still a very difficult equation to handle, and we therefore simplify the problem further by treating the charge Z on the ion as small, and expanding in powers of Z. Since we already have introduced a subscript to distinguish terms of first and second order in u, we have now to use two subscripts, of which the first indicates the order in u, the second the order in Z.

Then, for example,

$$n_0 = n_{00} + n_{01}$$
$$n_{01} = \frac{\partial n_{00}}{\partial E} V_{01} \qquad \text{(AII.5)}$$

We can immediately find V_{01} from Poisson's equation:

$$\nabla^2 V_{01} = -\frac{8\pi e^2}{h^3} V_{01} \int \frac{\partial n_{00}}{\partial E} 4\pi p m \, dE = \frac{4e^2 m p_F}{\pi \hbar^3} V_{01}$$
$$= \alpha^2 V_{01} \qquad \text{(AII.6)}$$

with the solution

$$V_{01} = -\frac{Ze^2}{r} e^{-\alpha r} \quad ; \quad \alpha^2 = \frac{4e^2 m p_F}{\pi \hbar^3} \qquad (AII.7)$$

$p_F = (2mE_F)^{1/2}$ is the Fermi momentum. Now return to equation (4) and make a Fourier transform for f:

$$f(\underline{p},\underline{r}) = \int e^{i\underline{k}\cdot\underline{r}} g(\underline{p},\underline{k})\, d^3\underline{k}$$

$$V(\underline{r}) = \int e^{i\underline{k}\cdot\underline{r}} v(\underline{k})\, d^3\underline{k} \qquad (AII.8)$$

so that (4) becomes:

$$\frac{i}{m}\underline{p}\cdot\underline{k}\, g(\underline{p},\underline{k}) - i\int d^3q\, \underline{q}\cdot\frac{\partial}{\partial \underline{p}} g(\underline{p},\underline{k}-\underline{q}) v_0(\underline{q}) + \frac{g}{\tau} - \frac{\bar{g}}{\tau} = -\frac{u}{\tau} p_z \delta(\underline{k}) + \frac{i}{m}\underline{p}\cdot\underline{k}\, v_1(\underline{k}) \qquad (AII.9)$$

We now carry out our intention of ordering all the quantities according to powers of Z, so that

$$g = g_0 + g_1 + \cdots \qquad (AII.10)$$

where g_0 is by definition the solution of (9) for $Z=0$ and must satisfy:

$$\frac{i}{m}(\underline{p}\cdot\underline{k})g_0 + \frac{1}{\tau}(g_0 - \bar{g}_0) = -\frac{u}{\tau} p_z \delta(\underline{k}) \qquad (AII.11)$$

The solution is

$$g_0 = -u p_z \delta(\underline{k}) \qquad (AII.12)$$

It is easy to see that (12) is a solution of (11), since the first term of (11) vanishes when multiplied by the δ-function this is also the only permissible solution, since the homogeneous solution corresponds to distributions which rise

exponentially in space in some direction (12) simply expresses the fact that, in the absence of the ion, the electrons will on the average be stationary in the lab frame, i.e. will move with a velocity -u in the co-moving frame.

To first order

$$\frac{i}{m}(\underline{p}\cdot\underline{k})g_1 + \frac{1}{\tau}(g_1-\bar{g}_1) = \frac{i}{m}\,\underline{p}\cdot\underline{k}\;v_{11} - iuk_z v_{01} \qquad \text{(AII.13)}$$

Here $v_{01}(\underline{k})$ is the Fourier transform of (7):

$$v_{01} = \frac{Ze^2}{2\pi^2}\,\frac{1}{\alpha^2+k^2} \qquad \text{(AII.14)}$$

In evaluating the first-order contribution to v_1 i.e. v_{11} we must note that each factor in (2) contains a contribution of first order in Z, so that

$$\nabla^2 v_{11} = -\frac{8\pi e^2}{h^3}\left\{\int\frac{\partial n_{00}}{\partial E}f_1 d^3\underline{p} + \int\frac{\partial n_{01}}{\partial E}f_0 d^3\underline{p}\right\} \qquad \text{(AII.15)}$$

However, the second term vanishes, since the integral of f_0 over the direction of $\underline{p}$ is zero by (12). The Fourier transform of (15) is then

$$k^2 v_{11} = -\frac{4e^2 m p_F}{\pi h^3}\,\bar{g}_1(\underline{k}, p_F) = -\alpha^2\bar{g}_1 \qquad \text{(AII.16)}$$

Using these results, we now can put (13) into explicit form:

$$\frac{i}{m}(\underline{p}\cdot\underline{k})g_1 + \frac{1}{\tau}g_1 = -\frac{i}{m}(\underline{p}\cdot\underline{k})\frac{\alpha^2}{k^2}\bar{g}_1 + \frac{1}{\tau}\bar{g}_1 + \frac{iuk_z}{2\pi^2}\,\frac{Ze^2}{\alpha^2+k^2} \qquad \text{(AII.17)}$$

with the solution:

$$g_1 = \frac{\left(-\frac{i}{m}\alpha^2 \frac{\underline{p}\cdot\underline{k}}{k^2} + \frac{1}{\tau}\right)\bar{g}_1 + \frac{iuk_z}{2\pi^2}\frac{Ze^2}{\alpha^2+k^2}}{\frac{i}{m}(\underline{p}\cdot\underline{k}) + \frac{1}{\tau}} \qquad \text{(AII.18)}$$

This is still an implicit equation, since it contains $\bar{g}_1$, but we can obtain an equation for $\bar{g}_1$ alone by averaging (18) over the direction of $\underline{p}$. Since the direction of $\underline{p}$ enters in (18) only in the form $\underline{p}.\underline{k}$, we write $\underline{p}.\underline{k} = pk\cos\theta = pks$, and the averaging then amounts to the operation $\frac{1}{2}\int_{-1}^{1} ds$.

The integrations are elementary and lead to

$$\bar{g}_1 = \frac{\gamma}{kl}\bar{g}_1 - \frac{\alpha^2}{k^2}\left(1-\frac{\gamma}{kl}\right)\bar{g}_1 + \frac{iuk_z}{2\pi^2}\frac{Ze^2}{\alpha^2+k^2}\frac{\gamma\tau}{kl} \qquad \text{(AII.19)}$$

where

$$\gamma = \tan^{-1}\frac{kp\tau}{m} = \tan^{-1}kl \qquad \text{(AII.20)}$$

l being the mean free path of an electron of momentum p_F.

We solve (19) for $\bar{g}_1$:

$$\bar{g}_1 = iu\frac{Ze^2}{2\pi^2}k_z\frac{k^2}{(k^2+\alpha^2)^2}\frac{\gamma\tau}{(kl-\gamma)} \qquad \text{(AII.21)}$$

By inserting this in (18) we have now found the solution to first order in u and in Z.

From this we can determine the force exerted by the

electrons on the ion.

$$F_z = Z\left(\frac{\partial V_{11}}{\partial z}\right)_{r=0} = iZ\int k_z v_{11}\, d^3\underline{k} = i\alpha^2 Z\int \frac{k_z}{k^2}\,\bar{g}_1\, d^3\underline{k}$$

$$= -\frac{uZ^2e^2\alpha^2}{2\pi^2}\int \frac{k_z^2\,\gamma\tau\, d^3\underline{k}}{(\alpha^2+k^2)^2(kl-\gamma)} \qquad \text{(AII.22)}$$

This integral diverges at large k. The reason is that for large k, i.e. for close collisions, perturbation theory is not applicable. This situation is familiar from the theory of atomic collisions, and since the divergence is only logarithmic one can get a reasonable answer by cutting off the integration at a maximum value of k corresponding to a collision in which the momentum transfer would be of the same order as the total momentum of the electron.

An exact evaluation of the integral would be cumbersome, but we can get a good approximation by using the fact that in practice αl is a large number. We may then divide the range of integration into three parts:

I. 0 to k_1, where $k_1 l$ is of the order of unity,
II. k_1 to k_2, where $k_2 l \gg 1$ but $k_2 \ll \alpha$
III. k_2 to k_3, where $k_3 \gg \alpha$, hence also $k_3 l \gg 1$

Write the force as

$$-\frac{uZ^2e^2\alpha^2}{2\pi^2}\,K \qquad \text{(AII.23)}$$

where

$$K = \frac{4\pi\tau}{3}\int \frac{k^4 dk}{(\alpha^2+k^2)^2}\,\frac{\gamma}{(kl-\gamma)} \qquad \text{AII.24)}$$

In region I, k^2 can be neglected by comparison with α^2, γ is a small number, and hence by (20)

$$kl - \gamma \sim \frac{1}{3}(kl)^3$$

The contribution to K from region I is therefore approximately

$$\frac{4\pi\tau}{3l^2\alpha^4} k_1^3 \simeq \frac{4\pi\tau}{3\alpha^4 l^5}$$

In region II, γ is practically $\pi/2$, and the contribution to K becomes

$$-\frac{\pi^2\tau}{6\alpha^4 l^5} + \frac{\pi^2\tau}{6\alpha^4 l} k_2^4$$

Finally for region III:

$$\frac{\pi^2\tau}{3l}\left\{\ln\left(1+\frac{k_3^2}{\alpha^2}\right) - \frac{k_3^2}{\alpha^2+k_3^2} - \ln\left(1+\frac{k_2^2}{\alpha^2}\right) + \frac{k_2^2}{\alpha^2+k_2^2}\right\} \simeq \frac{\pi^2\tau}{3l}\left\{\ln\frac{k_3^2}{\alpha^2} + \frac{2\alpha^2}{k_3^2} - 1 - \frac{k_2^4}{2\alpha^2}\right\}$$

Adding the contributions together the part from region I is seen to be negligible, the dependence on the value of k_2 cancels, and the leading term becomes:

$$\frac{\pi^2\tau}{3l}\left\{\ln\frac{k_3^2}{\alpha^2} - 1\right\}$$

Assuming the log to be of order unity (or rather, its excess over 1 to be of order unity) the force is

$$-\frac{u}{v_F}\frac{Ze^2\alpha^2}{6\pi}$$

This result applies to a moving ion with no external field. By using the identity relating the effect of motion with velocity, $u_E = Ee\tau/m$ to the effect of an external field E, we find the force due to the field

$$F_E \simeq - \frac{Z^2 e^3 \alpha^2 \tau E}{6\pi m v_F} \qquad \text{(AII·25)}$$

compared to the direct force ZeE. The ratio is $Ze^2\alpha^2\tau/6mv_F$. If one takes the screening radius of the order of the Bohr radius for hydrogen, then $e^2\alpha$ is of the order of the Fermi energy $\frac{1}{2}mv_F^2$, and this would make the ratio $Z\alpha l/12\pi$. The numerical factor is not reliably given by this estimate, but it is clear that, even for Z = 1, the first-order term in the force is not small.

REFERENCES

Bateman Manuscript Project
(Vol 1 McGraw-Hill, New York (1954))
"Tables of Integral Transforms"

R.G. Chambers
(Proc. Phys. Soc. A65 458 (1952))
"The Kinetic Formulation of Conduction Problems"

Alfred Coehn & Werner Specht
(Z. Physik 62 1 (1930))
"Uber die Beteiligung von Protonen an der Elektrizitätsleitung in Metallen.I.Nachweis durch Potentialmersungen"

A.K. Das
(D. Phil. Thesis, Oxford (1966))
"The effect of screening on an ion moving in an electron gas"

D.F. Dubois
(Ann. of Physics 7, 174 (1959))
"Electron Interations, Part I. Field Theory of a Degenerate Electron Gas"

V.B. Fiks
(Fiz. Tverdogo Tela 1, 16 (1959)
"English Translation. Sov. Phys. Solid State 1, 14 (1959)
"On the mechanism of the mobility of ions in metals"

J. Friedel & S. Bosvieux
(J. Phys. Chem. Solids 23 123 (1962))
"Sur l'electrolyse des Alliages Metalliques"

H.B. Huntington & A.R. Grone
(J. Phys. Chem. Solids 20 76 (1961))
"Current induced marker motion in gold wires"

H.B. Huntington & Siu-Chung Ho
(J. Phys. Soc. Japan 18 (Suppl. 2) 202 (1963))
"Electromigration in Metals"

E. Jahnke & F. Emde
(4th Ed. New York (1945)
"Tables of Functions"

D.F. Kalinovich
(Sov. Phys. Solid State 3, 812 (1961))
"Electrical Transport in Interstitial Solid Solutions"

C. Kittel
(Wiley New York (1963))
"Quantum Theory of Solids"

P.P. Kuz'menko
(Ukr. Fiz. Zh. 7, 117 (1962))

A.J. Maeland
(Can.J. Phys. 46, 121 (1968))
"A Neutron Diffraction Study of the α-phase in the Pd - Au - H and Pd - Au - D systems."

R.E. Peierls
(1955)
"Quantum Theory of Solids"

J.L. Routbort
(Phys. Rev. 176, 796 (1968))
(Electromigration in Zinc single crystals"

Von H. Wever
(Z. Electrochem. 60, 1170 (1956))
"Uberführungsversuche an festem Kupfer"

J.M. Ziman
(Clarendon Press, Oxford (1960))
"Electrons and Phonons"

J.M. Ziman
(Cambridge University Press (1954))
"Principles of the Theory of Solids"