

## Effect of correlations on electron momentum density in liquid metals

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**Abstract.** A scheme to calculate the electron momentum density in simple liquid metals, with the effect of *both* electron correlations and ionic potentials included, is given. This scheme is applied to the case of liquid aluminium. The results are substantially different from calculations considering only the ion potentials, and also from the results for a homogeneous electron gas of corresponding density.

**Keywords.** Electron momentum density; electron correlations; liquid metals.

### 1. Introduction

It has been noted (Chaddah and Sahni 1976) that the electron correlations are the probable cause of the long tail seen in experimental Compton profiles (CP). We are already aware of the well known calculation of Daniel and Vosko (1960) for a homogeneous interacting electron gas, which shows that electron correlations reduce the discontinuity in the electron momentum density (EMD) at  $K_F$ , and also introduce a long tail in it. It is interesting to explore if calculations for an inhomogeneous interacting electron gas show a large tail in the EMD. The problem becomes extremely complex for a crystalline solid but for a molten metal it is somewhat tractable and it turns out that one can perform numerical calculations within a reasonable approximation scheme. Accordingly, we present a scheme for calculating the EMD of a monoatomic molten metal, which includes the effects of both electron correlations and ionic potentials, and give the results of a calculation for molten Al. Our approach is essentially an extension of the Daniel Vosko scheme in which the ionic effects are included by following a formalism due to Edwards (1962). In a pioneering work in the study of electron states, Edwards developed a formalism for calculating the electron Green's function starting from the free electron Green's function and taking account of the perturbation because of ionic pseudopotentials. The perturbed Green's function  $G(\mathbf{k}, E)$  that he calculated can be used to obtain the EMD and the density of states:

$$n(\mathbf{k}) = -\frac{1}{\pi} \int_{\text{occupied states}} \text{Im } G^-(\mathbf{k}, E) dE \quad (1)$$

$$\text{and } \rho(E) = -\frac{1}{\pi} \int_{-\infty}^{\infty} \text{Im } G^-(\mathbf{k}, E) d^3 \mathbf{k} \quad (2)$$

where the superscript identifies the retarded Green's function. Among other things, Edwards showed that Ziman's theory of resistivity in liquid metals follows as an approximation to his own formulation. However, he did not perform any numerical calculations for  $n(\mathbf{k})$  or  $\rho(E)$ . Later Ballentine (1966) used this method to numerically obtain the EMD, and density of states, in liquid Al. Moreover, for reasons to be discussed in the next section, he also used a self-consistent procedure (often called the complex energy approximation) to evaluate the Green's function, and obtain the EMD (besides other electronic structure information) for liquid Al, Zn and Bi. Itami and Shimoji (1972) studied the electronic structure of many liquid metals and alloys using Ballentine's self-consistent procedure. Chan and Ballentine (1972) have recently used non-local pseudopotentials to obtain the electronic structure in liquid Bi, In and Hg. None of the above calculations has, however, attempted to include the effect of electron-electron correlations. Various other methods have been used to calculate the density of states in liquid metals, but they also do not consider correlations. To avoid digression, we will not discuss them here but shall concentrate on reviewing the work of Ballentine (1966), as this is of utmost relevance to us.

Our approach essentially consists of modifying the free electron propagator to include the effect of ion potential by the above method. This modified propagator which describes the 'unperturbed state'—with the electron-electron interactions playing the role of perturbations,—is then used for calculating the EMD following the same procedure as was used by Daniel and Vosko (1960). The numerical results for liquid Al, presented later in this paper, reveal that whereas the departure of the EMD from the unit step function is, for example, 0.05 at  $0.9K_F$  for a calculation following Ballentine, inclusion of correlations changes it to 0.15 at  $0.9K_F$ . It must be emphasized here that although the EMD can be measured by using either Compton scattering or positron annihilation, the electron correlation effects are not seen in the latter experiments (Carbotte and Kahana 1964). The reason for this is that the annihilating electron, because of the positron, appears partially neutral to the other electrons. Thus to directly test the above conclusions a CP study has to be made, and some efforts in this direction are under way. A preliminary report of this work has been published (Chaddah 1977).\*

## 2. Effect of ionic pseudopotentials on the electron Green's function

For investigating the behaviour of the conduction electrons, we adopt the usual model for a molten metal wherein these electrons are presumed to be detached from parent cores, and influenced by ionic pseudopotentials and mutual electron-electron interactions. The effect due to the pseudopotentials will be examined in this section, and the electron-electron interactions will be taken up in the following section.

Let  $V(\mathbf{r})$  be the total potential due to the ions, and  $G_0(E)$  be the free electron Green's function, then formal perturbation theory gives

$$G(E) = G_0(E) + G_0(E)VG_0(E) + G_0(E)VG_0(E)VG_0(E) + \dots \quad (3)$$

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\*The lower limit of integration in eq. (6) is  $-\infty$  and not zero as wrongly typed.

to be the electron Green's function in the presence of the ions. We now take  $V(\mathbf{r})$  to be the sum of spherically symmetric potentials centered at each of the  $N$  ions, i.e.

$$V(\mathbf{r}) = \sum_{\alpha} v(|\mathbf{r} - \mathbf{R}_{\alpha}|). \quad (4)$$

This results in factorisation of the matrix element

$$\langle \mathbf{k} | V | \mathbf{k}' \rangle = \langle \mathbf{k} | v | \mathbf{k}' \rangle \sum_{\alpha} \exp [i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{R}_{\alpha}] \quad (5)$$

and we may write eq. (3) in the momentum representation to get the diagonal component

$$\begin{aligned} G(\mathbf{k}, E) &= G_0(\mathbf{k}, E) + G_0(\mathbf{k}, E) V(\mathbf{k}, \mathbf{k}) G_0(\mathbf{k}, E) \\ &+ \sum_{\mathbf{k}'} G_0(\mathbf{k}, E) V(\mathbf{k}, \mathbf{k}') G_0(\mathbf{k}', E) V(\mathbf{k}', \mathbf{k}) G_0(\mathbf{k}, E) + \dots \end{aligned} \quad (6)$$

$$\text{with} \quad G_0(\mathbf{k}, E) = \frac{1}{E - (k^2/2)}. \quad (6a)$$

where we use units such as  $\hbar = 1$  and  $m = 1$ . The  $n$ th order term in eq. (6) can be written as

$$\begin{aligned} &\sum_{\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_{n-1}} G_0(\mathbf{k}, E) \langle \mathbf{k} | v | \mathbf{k}_1 \rangle G_0(\mathbf{k}_1, E) \langle \mathbf{k}_1 | v | \mathbf{k}_2 \rangle \dots \\ &\dots \langle \mathbf{k}_{n-1} | v | \mathbf{k} \rangle G_0(\mathbf{k}, E) C_n(\mathbf{k}_1 - \mathbf{k}, \mathbf{k}_2 - \mathbf{k}_1, \dots, \mathbf{k} - \mathbf{k}_{n-1}) \end{aligned} \quad (7)$$

where

$$C_n(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_n) = \sum_{\alpha, \beta, \dots, \omega} \exp [i(\mathbf{p}_1 \cdot \mathbf{R}_{\alpha} + \dots + \mathbf{p}_n \cdot \mathbf{R}_{\omega})]. \quad (8)$$

Equations (6), (7) and (8) show how the (perturbed) Green's function is modified by the pseudopotentials for a given microscopic configuration of ions. Now in any macroscopic sample of molten metal, there will be a conglomeration of various microscopic configurations and one must average over all of these, that is to say we must ensemble average the above equations. To obtain such an ensemble average of  $G(\mathbf{k}, E)$  we replace  $C_n$  by its ensemble average  $\overline{C}_n$ , and this involves the  $n$ -particle correlation function of the liquid. As a matter of fact the above equations, as they stand, equally apply for a solid or a molten metal. However, the ensemble averaging makes the numerical computations far more tractable for the latter. The perturbation series given by eq. (6) can be rearranged and summed to obtain

$$G(\mathbf{k}, E) = \left[ E - \frac{k^2}{2} - \Sigma(\mathbf{k}, E) \right]^{-1} \quad (9)$$

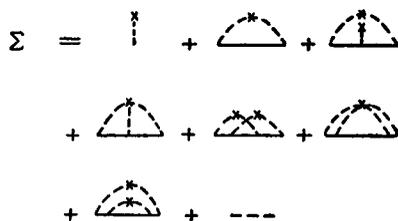


Figure 1. The self-energy of the electron,  $\Sigma$ , is the sum of all the irreducible diagrams. The full-line indicates the free electron propagator, while the dotted lines indicate interaction with the ionic potentials.

where  $\Sigma(\mathbf{k}, E)$ , the 'self-energy', is the sum of all the irreducible graphs and this is indicated in figure 1. To obtain the retarded Green's function one follows the standard procedure of adding an infinitesimal positive imaginary part to  $E$ . The 1st order contribution to  $\Sigma(\mathbf{k}, E)$  is just the average potential energy, which can be chosen as zero. The second order contribution is given by (Ballentine 1966)

$$\Sigma_2(\mathbf{k}, E) = \frac{n}{8\pi^3} \int d^3\mathbf{p} \frac{|u(\mathbf{k}-\mathbf{p})|^2 a(\mathbf{k}-\mathbf{p})}{E-(p^2/2)} \quad (10)$$

with

$$a(\mathbf{k}-\mathbf{p}) = \bar{c}_2(\mathbf{p}-\mathbf{k}, \mathbf{k}-\mathbf{p}),$$

and we will ignore higher order contributions to  $\Sigma(\mathbf{k}, E)$ . Note, however, that this does not mean that  $G(\mathbf{k}, E)$  contains only terms up to second order in  $v$ , rather it contains contributions to *all* orders due to a class of terms. In eq. (10),  $n$  is the ionic density;  $a$  is the fourier transform of the two-particle correlation function, or the structure factor; and  $u$  is the ionic pseudopotential. The angular integration in eq. (8) can be easily performed by using the spherical symmetry of  $a$  and  $u$ , and we get the real and imaginary parts as

$$\text{Re } \Sigma(k, E) = \frac{n}{4\pi^2 k} \int_0^\infty p dp [u(p)]^2 a(p) \ln \left| \frac{\frac{1}{2}(p-k)^2 - E}{\frac{1}{2}(p+k)^2 - E} \right| \quad (11)$$

$$\text{Im } \Sigma(k, E) = -\frac{n\pi}{8\pi^2 k} \int_{|k-\sqrt{E}|}^{k+\sqrt{E}} p dp [u(p)]^2 a(p). \quad (12)$$

Using eqs (9), (11) and (12) with appropriate values for the pseudopotential and the structure factor,  $\Sigma(k, E)$  and hence  $G(k, E)$  can be evaluated. Substituting the latter in eqs (1) and (2), one can obtain the EMD and the density of states. Ballentine found an anomaly at low energy, in the calculated density of states on using this procedure. He found from calculations based on the above formalism that for some positive values of  $k$  both the equations given below were satisfied.

$$\text{Im } \Sigma(\mathbf{k}, E) = 0 \quad (13)$$

$$\text{and } E - \frac{k^2}{2} - \text{Re } \Sigma(\mathbf{k}, E) = 0.$$



(i) choose a value of  $p_0$ , and using (15) and (16),

$$\text{Rl } F(E) = p_0^2/2 \quad (18)$$

(ii) From (16),  $\text{Im } F(E) = -\text{Im } \Sigma(P_0, E)$  and substituting for the imaginary part of  $\Sigma$  from eq. (17),

$$\begin{aligned} \text{Im } F &= \frac{n}{8\pi^2 p_0} \int_0^\infty p dp [u(p)]^2 a(p) \text{Im} \ln \left[ \frac{\frac{1}{2}(p+p_0)^2 - F}{\frac{1}{2}(p-p_0)^2 - F} \right] \\ &= \frac{n}{8\pi^2 p_0} \int_0^\infty p dp [u(p)]^2 a(p) \tan^{-1} \frac{2p_0 p \text{Im } F}{\frac{1}{4}p^4 - p_0^2 p^2 + (\text{Im } F)^2} \end{aligned} \quad (19)$$

where we have made use of eq. (18), and the arctan is fixed between  $-\pi$  and  $\pi$ . Equation (19) is solved numerically to obtain  $\text{Im } F$  as a function of  $p_0$ . With this, we know  $F$  and on using eq. (17) we can get  $\text{Rl } \Sigma(p_0, E)$  as

$$\begin{aligned} \text{Rl } \Sigma(p_0, E) &= -\frac{n}{8\pi^2 p_0} \int_0^\infty p dp [u(p)]^2 a(p) \\ &\quad - \frac{1}{2} \ln \left[ \frac{\left(\frac{p^2}{2} + p_0 p\right)^2 + (\text{Im } F)^2}{\left(\frac{p^2}{2} - p_0 p\right)^2 + (\text{Im } F)^2} \right] \end{aligned} \quad (20)$$

and finally obtain

$$E = \frac{p_0^2}{2} + \text{Rl } \Sigma(p_0, E). \quad (21)$$

We thus obtain  $E$  and  $F$  for various values of  $p_0$ . These are then inverted to write  $p_0$  and  $F$  as functions of  $E$  and upon substituting in eq. (17) we can obtain the complete function  $\Sigma(k, E)$ .

For the case of liquid Al, Ballentine used the pseudopotential of Heine and Abarenkov (1964) and the structure factor obtained by Gamertsfelder (1941). But, as also noted by Ballentine, this x-ray structure factor has a spurious peak at low momentum, and thus the calculated EMD will show an exaggerated departure from the free electron case. So for our calculation we decided to use a more accurate value of the structure factor determined by Fessler *et al* (1966) using neutron scattering. Of course, as a check on our computer program we first reproduced the earlier results of Ballentine using Gamertsfelder's structure factor.

For the pseudopotential we again used the Heine-Abarenkov pseudopotential previously used by Ballentine. The potential has been generated in a local approximation, and is screened using the static Hartree dielectric function which is slightly modified, following Heine and Abarenkov, to account for the conduction electrons being orthogonal to core states. We have used the same parameters, and followed the same local approximation scheme, as were employed by Ballentine. We should

**Table 1.** A comparison of various calculations for the EMD for liquid Al.

$k/k_f$	EMD: $n(k)$		
	With only electron-ion interactions and no correlations (following Ballentine)	With both electron-ion interactions and correlations (this scheme)	With only correlations and no electron-ion interaction (from Daniel and Vosko)
0.1	0.98	0.97	0.97
0.5	0.98	0.96	0.96
0.7	0.98	0.93	0.94
0.8	0.97	0.91	0.93
0.9	0.95	0.85	0.90
1.1	0.047	0.09	0.06
1.2	0.015	0.036	0.029
1.3	0.007	0.02	0.02

emphasize that at this stage no effort is made to include the effect of correlations among the conduction electrons.

Using this potential and the structure factor of Fessler *et al* (1966) we followed Ballentine's self-consistent procedure, and obtained the EMD. Our results are given in table 1. As expected, this is more free electron-like than what was obtained by Ballentine using the structure factor due to Gamertsfelder. The value of  $\Sigma(k, E)$  obtained in our calculation were used in what follows.

### 3. Inclusion of correlation effects

With the values of  $\Sigma(k, E)$  obtained above, eq. (9) gives the Green's function for electrons by the ionic potentials. In this section we consider the effect of coulombic interactions amongst these 'modified' electrons.

We now make the approximation to eq. (9), valid in the region near the pole of the Green's function,

$$\begin{aligned}
 G(k, E) &= \frac{1}{E - \frac{k^2}{2} - \Sigma(k, E)} \simeq \frac{1}{E - \frac{k^2}{2} - \sum \left( k, \frac{k^2}{2} + \Sigma \right)} \\
 &\simeq \frac{1}{E - \frac{k^2}{2} - \sum \left( k, \frac{k^2}{2} \right)} \quad (23)
 \end{aligned}$$

and we will use for convenience the notation

$$\sum_k \equiv \sum \left( k, \frac{k^2}{2} \right). \quad (24)$$

We have thus assumed that the modified electrons have energy  $\epsilon_k = (k^2/2) + \text{Re } \Sigma_k$  and a damping  $\gamma_k = \text{Im } \Sigma_k$ . Now, for a long-lived quasiparticle having a Green function given by eq. (9), we have (see Fetter and Walecka 1971).

$$\epsilon_k = \frac{k^2}{2} + \text{Re } \Sigma(k, \epsilon_k)$$

$$\gamma_k = \frac{\text{Im } \Sigma(k, \epsilon_k)}{\left[ 1 - \text{Re} \left. \frac{\partial \Sigma(k, \omega)}{\partial \omega} \right|_{\omega = \epsilon_k} \right]}$$

For

$$\left. \frac{\partial \Sigma(k, \omega)}{\partial \omega} \right|_{\omega = \epsilon_k} \ll 1$$

we get back the approximation made in eqs (23) and (24). Such approximations, where the  $E$ -dependence of  $\Sigma(\mathbf{k}, E)$  is finally ignored, are made when we use the momentum to label decaying quasiparticle states. We attempt to look at these states as simultaneous eigenstates of the hermitian momentum operator and a non-hermitian Hamiltonian. If such simultaneous eigenstates are to form a complete set (as desired here, and in complex band structure calculations) then the momentum operator and the complex Hamiltonian must commute. This straightaway implies that both the real and the imaginary parts ( $\epsilon$  and  $\gamma$ ) of the complex Hamiltonian must be functions of  $\mathbf{k}$  alone. In our case the complex energy, which is a function of  $\mathbf{k}$  alone, is

$$\epsilon_{|\mathbf{k}|} = \frac{k^2}{2} + \Sigma_k.$$

We are now ready to consider the correlation effects and to calculate the EMD following Daniel and Vosko (1960). Following their procedure, we add to the actual Hamiltonian a fictitious infinitesimal term to get

$$H_\lambda(k) = H_0 + \lambda k_F^2 \sum_{\mathbf{p}+\mathbf{q}} a_{\mathbf{p}+\mathbf{q}}^+ a_{\mathbf{p}+\mathbf{q}} \delta_{|\mathbf{p}+\mathbf{q}|, k} - \lambda k_F^2 \sum_{\mathbf{p}} a_{\mathbf{p}} a_{\mathbf{p}}^+ \delta_{|\mathbf{p}|, k}. \quad (25)$$

Here  $\lambda$  is an infinitesimal parameter, and  $a_{\mathbf{k}}^+$  ( $a_{\mathbf{k}}$ ) is the creation (annihilation) operator for an electron with momentum  $\mathbf{k}$  (but with a propagator given by eq. (23)). The EMD  $n(k)$  of the system is given by the ground state expectation value of  $a_{\mathbf{k}}^+ a_{\mathbf{k}}$ . We use in eq. (25), and in what follows, the convention

$$|\mathbf{p}| < k_F \text{ and } |\mathbf{p} + \mathbf{q}| > k_F. \quad (26)$$

The momentum density is then calculated as follows. The ground energy  $E_\lambda(k)$  of this fictitious Hamiltonian  $H_\lambda(k)$  is evaluated by treating the perturbation, caused by electron interactions and the fictitious term, in the random phase approximation,

using the technique of Gell-Mann and Brueckner (1957) to sum the diagrams for electron-hole pair excitations. The effect of the electron-electron interaction till the Hartree-Fock term is included in the pseudopotential, and only diagrams corresponding to interactions beyond these are considered. Also, as pointed out by Daniel and Vosko (1960), exchange graphs give comparatively negligible contribution near the Fermi surface and are ignored. The EMD is then evaluated using  $E_\lambda(k)$  through the equation

$$P(k) = \lim_{\lambda \rightarrow 0} \frac{\pi^3}{\Omega k_F^3} \frac{1}{k^2} \frac{\partial E_\lambda(k)}{\partial \lambda}. \quad (27)$$

Equation (27) already takes account of the number of states per unit  $k$ -space, and the EMD is given by

$$\begin{aligned} n(k) &= P(k) \text{ for } k > k_F \\ &= 1 + P(k) \text{ for } k < K_F. \end{aligned} \quad (28)$$

We have implicitly assumed that the ground state of the unperturbed system is a Fermi vacuum. This is justified as  $\text{Re } \Sigma_k$  is a smooth function of  $k$  and so all states from  $k=0$  to  $K_F$  are occupied, where  $K_F$  satisfies

$$\frac{K_F^2}{2} + \text{Re } \Sigma_{K_F} = E_F. \quad (29)$$

Moreover, it is clear from eq. (27) that what matters (in the evaluation of the EMD) is the  $\lambda$ -dependent part of the ground state energy, and this is obtained from the electron-hole pair excitations. Consequently, what is really important is to fully include the effect of ionic potentials in the corresponding propagators, and this is what we do by using the propagators given by eq. (23).

Gell-Mann and Brueckner (1957) had obtained the correlation energy for a homogeneous electron gas in the random phase approximation. The problem is to sum to all orders the contributions, to the ground state energy, of electron-hole excitations with a momentum transfer  $\mathbf{q}$ . They rewrote the energy denominators in a temporal representation, with suitable electron propagators, and they obtained the sum of all diagrams in a given order as a single integral. The contributions from various orders then form a geometric series, and can be summed in a closed form. Using the Gell-Mann and Brueckner technique, and following the procedure of Daniel and Vosko (1960), we get

$$\begin{aligned} E_\lambda(k) &= -\frac{1}{2} \frac{\Omega k_F^3}{8\pi^3} \frac{1}{2\pi} \int_{|\mathbf{p} + \mathbf{q}| > |} q d^3\mathbf{q} \sum_{n=2}^{\infty} \frac{(-1)^n}{n} \\ &\int_{-\infty}^{\infty} \left[ \frac{\alpha Q(u, q, k)}{q^2} \right]^n du \end{aligned} \quad (30)$$

with units  $K_F = 1$  in eq. (30) and in what follows, and with

$$Q(u, q, k) = \int_{|\mathbf{p}| < 1} d^3\mathbf{p} \int_{-\infty}^{\infty} dt \exp(-ituq) \exp[-|t|(\epsilon_{|\mathbf{p}+\mathbf{q}|} - \epsilon_{|\mathbf{p}|} + \lambda(\delta_{|\mathbf{p}+\mathbf{q}|, k} - \delta_{|\mathbf{p}|, k})], \quad (31)$$

$$\alpha = \frac{e^2}{\pi^2 K_F} \quad (32)$$

and where  $\epsilon_{|\mathbf{k}|}$  gives the energy at which the pole occurs in  $G(k, E)$ . From eq. (23)

$$\epsilon_{|\mathbf{k}|} = \frac{k^2}{2} + \Sigma_k. \quad (33)$$

The sign of  $\text{Im } \Sigma_k$  is chosen suitably for  $k > 1$  and  $k < 1$ , and also for  $t > 0$  and  $t < 0$ . To first order in  $\lambda$  we can write

$$E_\lambda(k) = E_0 + \lambda E_1(k)$$

where

$$E_1(k) = \frac{\Omega k_F^3}{8\pi^3} \frac{1}{4\pi} \int \frac{d^3\mathbf{q}}{q} \int_{-\infty}^{\infty} du \alpha Q_1 \sum_{n=1}^{\infty} \left( \frac{-\alpha Q_0}{q^2} \right)^n \quad (34)$$

$Q_0$  and  $Q_1$  are given by

$$Q_0(u, q) = \int_{\substack{|\mathbf{p}| < 1 \\ |\mathbf{p}+\mathbf{q}| > 1}} d^3\mathbf{p} \int_{-\infty}^{\infty} dt \exp(-ituq) \exp[-|t|(\epsilon_{|\mathbf{p}+\mathbf{q}|} - \epsilon_{|\mathbf{p}|})] \quad (35)$$

$$Q_1(u, q, k) = \int d^3\mathbf{p} (\delta_{|\mathbf{p}+\mathbf{q}|, k} - \delta_{|\mathbf{p}|, k}) \int_{-\infty}^{\infty} dt \exp(-ituq) |t| \cdot \exp[-|t|(\epsilon_{|\mathbf{p}+\mathbf{q}|} - \epsilon_{|\mathbf{p}|})] \quad (36)$$

Putting  $\sigma = \frac{1}{2}q^2 + \mathbf{q} \cdot \mathbf{p} + \text{Re } \Sigma_{|\mathbf{p}+\mathbf{q}|} - \text{Re } \Sigma_{|\mathbf{p}|}$  (37)

and  $\beta = uq - \text{Im } \Sigma_{|\mathbf{p}+\mathbf{q}|} - \text{Im } \Sigma_{|\mathbf{p}|}$  (38)

where  $\text{Im } \Sigma > 0$ , we get

$$Q_0(u, q) = 2 \int d^3\mathbf{p} \frac{\sigma}{\sigma^2 + \beta^2} \quad (39)$$

$$Q_1(u, q, k) = -2 \int d^3\mathbf{p} (\delta_{|\mathbf{p}+\mathbf{q}|, k} - \delta_{|\mathbf{p}|, k}) \frac{\sigma^2 - \beta^2}{[\sigma^2 + \beta^2]^2}. \quad (40)$$

We finally get from eqs (27) and (34),

$$P(k) = \frac{1}{4\pi k^2} \int q dq \int_0^\infty du \alpha Q_1(u, q, k) \left[ \frac{q^2}{q^2 + \alpha Q_0(u, q)} - 1 \right] \quad (41)$$

where the limits of  $q$  integration are from  $(1-k)$  to  $\infty$  for  $k < 1$ , and from  $(k-1)$  to  $(k+1)$  for  $k > 1$ .

The problem of calculating  $n(k)$  reduces to evaluating the above integrals, and this is discussed in the next section.

#### 4. Computational details and results

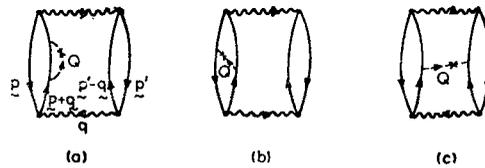
We will now discuss how to evaluate the EMD in a liquid metal using the preceding theory. To evaluate  $P(k)$ , we first need to calculate  $Q_0$  and  $Q_1$ , and for this we use the values of  $\Sigma_k$  whose computation was described in section 2. We performed the double integrations (over  $p$  and  $\theta$ ) in eqs (39) and (40) numerically and obtained  $Q_0$  and  $Q_1$  for various  $u$ ,  $q$  and  $k$ . The calculation was tested by taking  $\Sigma \equiv 0$ , and reproducing Daniel and Vosko's free electron results with  $\alpha = 0.11$ . In evaluating  $P(k)$  we exploited one simplifying feature viz. for large values of either  $q$  or  $u$ ,  $Q_0$  and  $Q_1$  are almost independent of  $\Sigma$ . We may therefore simplify the evaluation of eq. (41) by splitting the range of integrals into two regions: Region I where  $u$  and  $q$  are both less than some large but finite value  $\xi$  (taken as 4.5 in our case) and Region II where either  $u$  or  $q$  (or both) exceed  $\xi$ . Since in the latter region  $Q_0$  and  $Q_1$  are almost independent of  $\Sigma$  (including  $\Sigma \equiv 0$ ), the contribution to  $P(k)$  from this region may as well be obtained for the free electron case (i.e.  $\Sigma = 0$ ). Thus the  $\Sigma$ -dependence needs careful consideration only for Region I. The contribution to  $P(k)$  from this region is designated as  $P'(k)$ , and from Region II as  $R(k)$ . In our computation we evaluated  $R(k)$  by calculating  $P'(k)$  for the free electron case (i.e.  $\Sigma \equiv 0$ ) and subtracting this value from the results of Daniel and Vosko (with  $\alpha = 0.11$ ). We next obtained  $P'(k)$  for molten Al by actual numerical integration, and deduced  $P(k)$  by

$$P(k) = P'(k) + R(k). \quad (42)$$

The EMD  $n(k)$  is then obtained from eq. (28). The results from our scheme are given in table 1. For comparison, we have also given the results for a free electron gas of corresponding density. We have ignored the effect of temperature on the electron occupancies, since it causes a comparatively negligible change.

As is evident from the tabulated results, when the effect of both the ionic and correlation effects is included, the deviation of the EMD from the unit step-function is more than what either of the earlier schemes (which ignore one or the other of these effects) yields. We may add that our scheme can also be used to study correlation effects in anisotropic materials, though the computational effort required would go up enormously.

We would like to draw attention to an earlier attempt to study the EMD of an inhomogeneous interacting electron gas. Eisenberger *et al* (1972) had calculated the EMD in those pure metals where the smallest reciprocal lattice vector  $|\mathbf{G}| > 2K_F$ ,



**Figure 3.** We have followed the convention that  $|p| > p_F$  and corresponds to a 'hole' while  $|p \pm q| > p_F$  and corresponds to a particle.  $Q$  is the momentum transferred in an electron-ion interaction. The diagrams correspond to (a) electron self-interaction; (b) electron-hole interaction; and (c) electron-electron interaction, mediated by an ion.

in particular for Li and Na. They treat the electronic correlation 'exactly' (in the spirit of Daniel and Vosko 1960) and treat the inhomogeneous potential effect to second order of perturbation. In our calculation for a liquid metal, the effect of ions is considered to the second order of irreducible diagrams. This is well beyond the second order of perturbation. Further, in view of a large number of Green's function calculations for disordered solids, the electron self-energies obtained to a high degree of accuracy can be used in our scheme to obtain EMD's for other inhomogeneous interacting electron systems.

Before concluding we must note that in this scheme the ionic potentials are explicitly included only in the single electron Green's function, and consequently some many particle interactions are ignored. Though we include diagrams of the form shown in figure 3(a), electron-ion-electron interactions of the form shown in figure 3(b) are ignored. Such an ionic interaction will be accounted for if one starts with a two-electron Green's function, or in a many-body calculation which includes both ion-electron and electron-electron interactions *simultaneously*. In this case, however, the contribution from (a) is larger as one is allowed all values of momentum transfer  $Q$  to the ion. In (b) one starts with an electron-hole pair and the magnitude of  $Q$  is restricted since both the annihilating electrons cannot lie outside the Fermi sphere. Such restrictions on the available phase space do not apply for diagrams shown in figure 3(c), but their contribution cannot be evaluated by the present scheme.

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