Electron–electron correlations in liquid s–p metals

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Abstract

We present calculations for the valence electron–electron structure factor in liquid Mg near freezing, assuming knowledge of the jellium result. On the basis of this, we predict significant corrections to jellium short-range correlations in liquid s–p metals and in particular an increase in the electron–electron contact probability.

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1. Background and outline

Egelstaff *et al* [1] pointed out that a pure liquid metal with a well-defined valency could be fruitfully investigated as a two-component system of ions (i) and valence electrons (v). Thus by analogy, say with the classical molten salt, NaCl, three pair correlation functions are needed to characterize the structure. The first of these, $S_{ii}(k)$, is directly accessible by neutron scattering. While in principle, the remaining correlation functions $S_{iv}(k)$ and $S_{vv}(k)$ are also experimentally accessible by combining knowledge of $S_{ii}(k)$ with x-ray and electron diffraction studies, for Mg $S_{iv}(k)$ has become available recently by the computer simulation studies of de Wijs *et al* [2]. Thus, we present calculations for the remaining partial structure factor $S_{vv}(k)$.

The outline of the paper is then as follows. In section 2 the relevant theoretical results are briefly summarized, followed by numerical results on Mg in section 3. Section 4 treats corrections to jellium short-range correlations with results for Na and Mg. We conclude in section 5 with a summary of the main results and some proposals for future directions.

2. Theory: perturbation result for $S_{vv}(k)$ to second order in the electron–ion pseudopotential v_{iv}

Cusack *et al* [3] obtained the result that to second order in the (weak) electron–ion pseudopotential $v_{iv}(k)$, the correction $\delta S(k)$ to the (assumed known) jellium structure factor

$S_{vv}^{jell}(k)$, because of the ionic background, consists of two terms which we shall simply label by 1 and 2

$$\delta S(k) = \delta S_1(k) + \delta S_2(k). \tag{1}$$

The first correction $\delta S_1(k)$ is local in the ionic structure factor and is given by

$$\delta S_1(k) = \frac{1}{Z_v} \left| \pi(k) \frac{v_{iv}(k)}{\epsilon(k)} \right|^2 S_{ii}(k) \tag{2}$$

where Z_v denotes the valency, $\pi(k)$ the proper jellium polarization and $\epsilon(k)$ the static dielectric function given by $\epsilon(k) = 1 - v(k)\pi(k)$ with $v(k) = \frac{4\pi}{k^2}$ representing the bare Coulombic interaction. As was pointed out by, e.g., March and Murray [4], the resultant electron density profile when one disturbs a uniform electron gas of density ρ_v^0 with a weak spherically symmetric pseudopotential is given in linear response by

$$\rho_v(r) = \rho_v^0 + \int F(|\mathbf{r} - \mathbf{r}'|)V(r)\,d\mathbf{r} \tag{3}$$

where the response function $F(r)$ is simply the Fourier transform of the proper polarization $\pi(k)$ and $V(r)$ is the screened pseudopotential. Hence, the correction $\delta S_1(k)$ can be rewritten as

$$\delta S_1(k) = \frac{|\tilde{\rho}_v(k)|^2}{Z_v} S_{ii}(k) \tag{4}$$

with $\tilde{\rho}_v(k)$ being the linear response approximation to the Fourier transform of the displaced density profile around every ion, commonly called the 'form factor'. The term $\delta S_1(k)$ can then be interpreted as the correlation that results between electrons because they form neutralizing shells around the correlated ions.

The second correction term $\delta S_2(k)$ is given by

$$\delta S_2(k) = \frac{1}{2Z_v} \frac{1}{(2\pi)^3} \int S_{ii}(q)|v_{iv}(q)|^2 \chi_4(\mathbf{k}, -\mathbf{k}; -\mathbf{q}, \mathbf{q})\,d\mathbf{q} \tag{5}$$

where $\chi_4(\mathbf{k}, -\mathbf{k}; -\mathbf{q}, \mathbf{q})$ is the interacting four-body jellium response function which we calculated using the expression derived by Cusack *et al* [3] from the density functional theory.

3. Numerical results

In order to test the applicability of some of the main functions involved, we first calculated a quantity closely related to $\delta S_1(k)$, namely the ion–valence structure factor $S_{iv}(k)$, which to first order is given by [5]

$$S_{iv}(k) = \frac{1}{\sqrt{Z_v}} \left(\pi(k) \frac{v_{iv}(k)}{\epsilon(k)} \right) S_{ii}(k). \tag{6}$$

Figure 1 compares results for liquid Mg near freezing using equation (6) to the computer simulation result of de Wijs *et al* [2]. For the dielectric function a local field correction in the Hartree–Fock approximation [6] was used. The pseudopotential was calculated using the Ashcroft [7] empty core approximation with the standard Mg core radius value $R_c = 1.39a_0$, and the ion–ion structure factor $S_{ii}(k)$ was approximated by x-ray data at $T = 680$ K of the IAMP database [8]. Very good agreement over a substantial range of k-values is obtained.

The two constituents $\delta S_1(k)$ and $\delta S_2(k)$ are shown for liquid Mg in figure 2. The overall magnitude of both corrections is considerably increased compared to Na, but the main features are the same as those obtained by Cusack *et al* [3]. In particular we note that $\delta S_2(k \to 0) = 0$
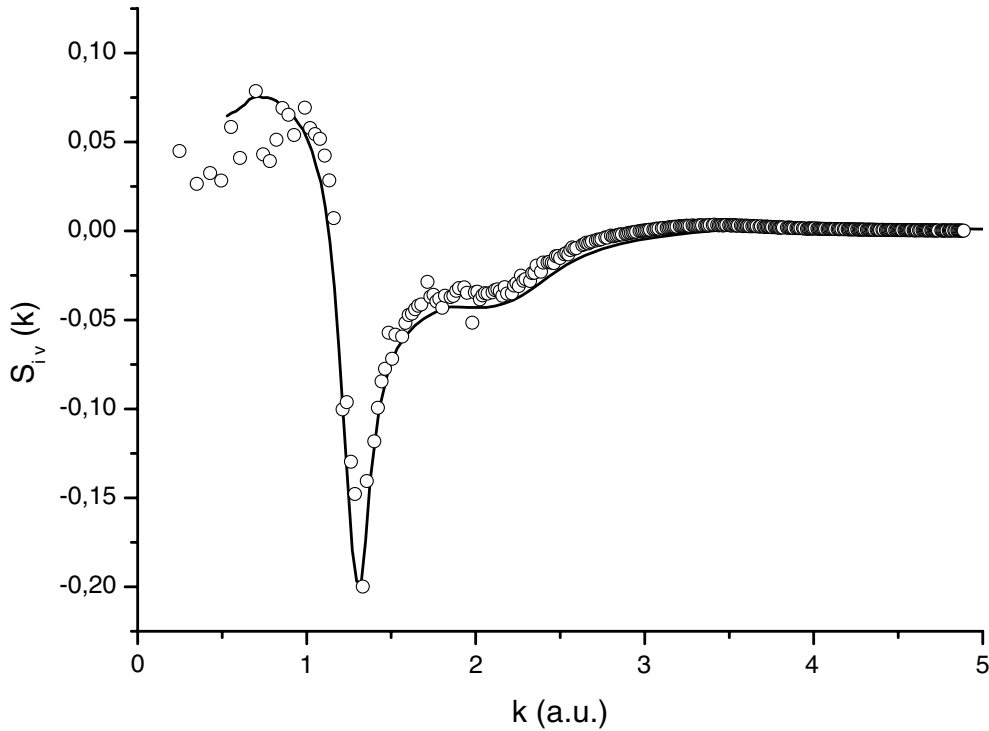
Figure 1. Ion–valence structure factor $S_{iv}(k)$ for liquid Mg. Circles are result from computer simulation of de Wijs *et al* [2], and solid line is linear response result.

and $\delta S_1(k \to 0) = Z_v S_{ii}(0)$ so that the normalization condition discussed in equation (10) is fulfilled. The pronounced peak in $S_{iv}(k)$ and in the first correction $\delta S_1(k)$ stems directly from the principal peak in $S_{ii}(k)$. The features of both peaks depend crucially on the position of the first node in the pseudopotential relative to the position of the principal peak in $S_{ii}(k)$. Because the pseudopotential appears squared in the expression for $\delta S_1(k)$, the antiphase behaviour of $S_{iv}(k)$ with respect to $S_{ii}(k)$ is not reproduced in $\delta S_1(k)$.

4. Corrections to jellium short-range electron–electron correlations

4.1. The electron–electron contact probability in a liquid metal

From the relation between the electronic pair correlation function $g_{vv}(r)$ and the structure factor $S_{vv}(k)$

$$g_{vv}(r) = 1 + \frac{1}{(2\pi)^3 \rho_v^0} \int (S_{vv}(k) - 1) \, e^{-i\mathbf{k}\cdot\mathbf{r}} \, d\mathbf{k} \qquad (7)$$

it is straightforward to calculate the change $\delta g_{vv}(0)$ in the pair correlation function at the origin from its jellium value. We performed calculations for liquid Na ($r_s \approx 4$) and Mg ($r_s \approx 2.8$) near freezing and the results are listed in table 1. The corrections are significant and were found to be positive; the effect of the ionic background tends to 'fill up' the jellium exchange-correlation hole at the origin to some extent. With decreasing r_s, the magnitude of the first correction $\delta g_{vv}^1(r)$ was found to increase significantly while the second correction $\delta g_{vv}^2(r)$ remained nearly the same.
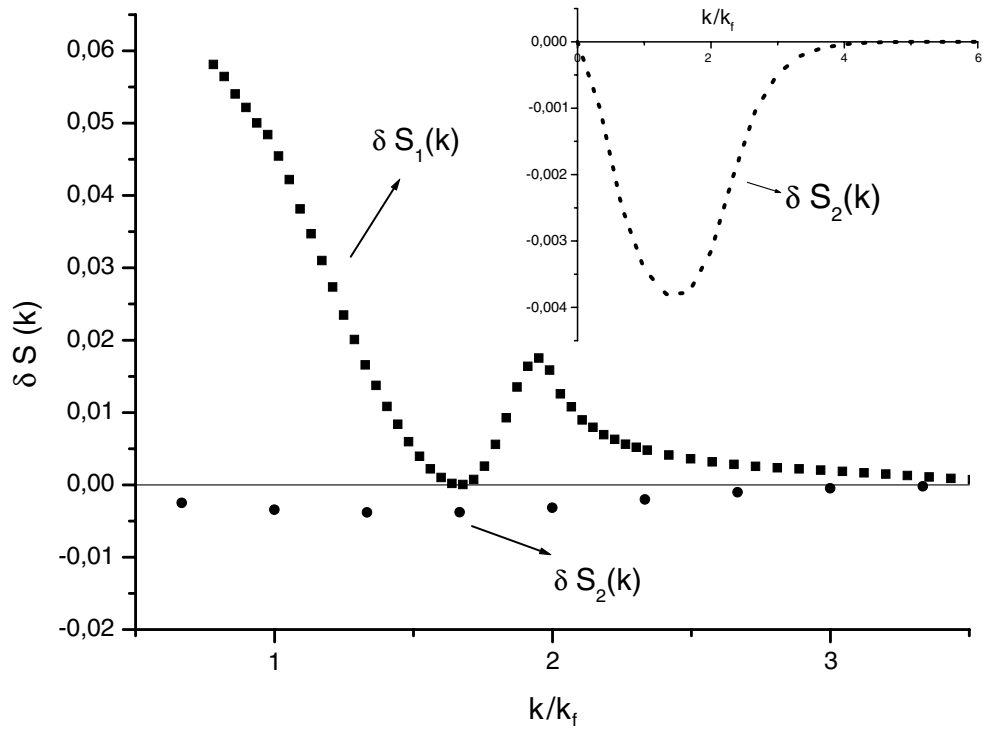
Figure 2. Corrections $\delta S_1(k)$ and $\delta S_2(k)$ to the jellium structure factor for liquid Mg. Inset shows $\delta S_2(k)$ on a more appropriate scale.

Table 1. Corrections to $g_{vv}^{jell}(0)$ in liquid Na and Mg near freezing. Contributions from δS_1 and δS_2 are given by $\delta g_{vv}^1(0)$ and $\delta g_{vv}^2(0)$ respectively. For comparison, the last row presents the contribution of correlation to $g_{vv}^{jell}(0)$ in jellium as obtained from equation (8). Total correction $\delta g_{vv}(0)$ adds up to 5% and 20% of $g_{vv}^{corr}(0)$ for Na and Mg respectively.

	Na ($r_s \approx 4$)	Mg ($r_s \approx 2.8$)
$\delta g_{vv}^1(0)$	+0.058	+1.102
$\delta g_{vv}^2(0)$	−0.040	−0.030
$\delta g_{vv}(0) = \delta g_{vv}^1(0) + \delta g_{vv}^2(0)$	+0.018	+0.072
$\delta g_{vv}^{corr}(0)$	−0.420	−0.381

It is useful to compare the magnitude of the corrections obtained above to those when taking into account electron correlation in jellium. From phase-shift analysis, Overhauser [9] obtained the following approximate result for the correction to $g_{vv}^{jell}(0)$ due to correlation

$$\delta g_{vv}^{corr}(0) = \frac{32}{(8+3r_s)^2} - \frac{1}{2}. \tag{8}$$

The results from this formula are also listed in table 1. For Na we see that the correction amounts to only 5% of that due to correlation, whereas for Mg almost 20% of the correlation hole at the origin is 'filled up' because of the ionic background. Although this does not follow

straightforwardly from the theory of Cusack *et al* [3], obviously the obtained corrections $\delta g_{vv}(0)$ can apply only between electrons with opposite spins and cannot exceed the correction $\delta g_{vv}^{corr}(0)$ in order not to violate the Pauli exclusion principle.

Whereas the magnitude of the corrections is clearly surprising, the sign of the correction is not. This is because the 'exchange-correlation' hole in a liquid metal is on average less deep compared to jellium. This can easily be seen from the normalization condition for $g_{vv}(r)$ which is determined by the request that any perturbing charge inserted in a conducting medium must be completely screened. In jellium this leads to the condition

$$\rho_v^0 \int \left(g_{vv}^{jell}(r) - 1 \right) dr = -1 \tag{9}$$

whereas in a liquid metal, where the positive ions contribute to the screening, this implies

$$\rho_v^0 \int \left(g_{vv}(r) - 1 \right) dr = -1 + Z_v S_{ii}(0) \tag{10}$$

where $S_{ii}(0)$ is typically of the order of 0.02.

4.2. The electron–electron cusp condition

Having indicated directly above the way in which significant changes in $g_{vv}(0)$ result from the corrections to the structure factor, it is natural to investigate if the jellium cusp relation as obtained by Kimball [10]

$$\left. \frac{\partial g_{vv}^{jell}(r)}{\partial r} \right|_{r=0} = -\frac{1}{a_0} g_{vv}^{jell}(0) \tag{11}$$

is modified when the above corrections are taken into account. We therefore turn to the limiting behaviour of the correction terms $\delta S_1(k)$ and $\delta S_2(k)$ when k tends to infinity. Regarding the first correction $\delta S_1(k)$, we can make analytic progress assuming that $\tilde{\rho}_v(k)$ represents the *exact* valence density profile. The result of Carlsson and Ashcroft [11] generalizing Kato's theorem [12] to continuum states then gives the nuclear cusp relation

$$\left. \frac{\partial \rho_v(r)}{\partial r} \right|_{r=0} = -\frac{2Z_v}{a_0} \rho_v(0) \tag{12}$$

where the origin $r = 0$ now refers to an ionic centre. This directly implies from equation (4)

$$\delta S_1(k)|_{k \to \infty} = \frac{1}{Z_v} \left(8\pi \rho_v^0 \left[\frac{2Z_v}{a_0} \rho_v(0) \right] \right)^2 \frac{1}{k^8}. \tag{13}$$

From our numerical calculations on Na and Mg, the second correction $\delta S_2(k)$ was found to tend to zero slightly faster than the predicted k^{-8} behaviour of $\delta S_1(k)$, namely proportional to k^{-10}, and so the first correction $\delta S_1(k)$ will dominate at large k. This leads to

$$\delta g_{vv}(r)|_{r \to 0} = \delta g_{vv}(0) - \frac{8\pi}{(2\pi)^3 \rho_v^0 Z_v} \left(8\pi \rho_v^0 \left[\frac{2Z_v}{a_0} \rho_v(0) \right] \right)^2 r^5 \tag{14}$$

and we conclude that the coefficient of the first-order term in the small r expansion of $g_{vv}(r)$ in a liquid s–p metal remains determined by the jellium value $g_{vv}^{jell}(0)$.

5. Summary and possible future directions

Calculations were performed for the valence electron–electron structure factor $S_{vv}(k)$ in s–p liquid metals, especially Mg, assuming knowledge of the jellium result. On the basis of

these results a significant increase in $g_{vv}(0)$ was found. We stress that this arises from a partial cancellation of two terms of opposite sign and that our quantitative results may change somewhat depending on the approximation to χ_4. However, since both terms tend to differ by over a factor 3 with decreasing r_s, we are confident that our conclusion will remain unchanged at least qualitatively. The jellium cusp relation remains valid in a liquid metal, the first correction appearing only to fifth order in r.

As a natural continuation of the present work, a detailed study of intermediate- and long-range corrections to $g_{vv}^{jell}(r)$ is of interest for future work. In contrast to the short-range behaviour, these are expected to depend sensitively on the detailed and possibly singular structure of χ_4.

Finally, experimental determination of $S_{vv}(k)$ following the pioneering proposal of Egelstaff *et al* [1] is obviously of great interest and remains an important challenge for future work.

Acknowledgments

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