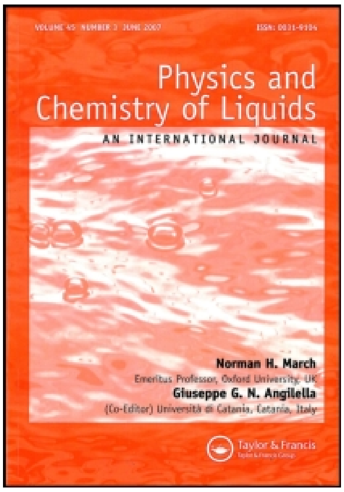

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Small *k*-behaviour of the Structure Factor of Simple Liquid Metals and Electron Correlations

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Letter

Small *k*-behaviour of the Structure Factor of Simple Liquid Metals and Electron Correlations

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Recent X-ray scattering data provides circumstantial evidence in support of the presence of a linear term in the small *k*-behaviour of the structure factor of simple liquid metals.

The analysis of such data requires the liquid to be described as a binary mixture of electrons and ions, in which case qualitative arguments show that electron correlations are responsible for the above behaviour.

In a recent publication, Matthai and March[1] (hereinafter to be referred as M-M) have inferred, by analysing the experimental results of Greenfield *et al.*[2], that the small *k*-behaviour of the structure factor $S(k)$ in liquids Na and K is dominated by a linear term, i.e.

$$S(k) - S(0) = a_1 k + a_2 k^2 + a_3 k^3 \tag{1}$$

where $S(0) = nk_B T\kappa_T$ is the long wavelength limit of the structure factor, with n the ions number density, k_B the Boltzmann constant, T the temperature and κ_T the isothermal compressibility. The coefficients a_i are functions of the thermodynamic state, and the analysis of M-M suggests that a_3 is approximately zero.

M-M explain the above behaviour in terms of collective (phonons) excitations in liquid metals, which are known to exist in, say, liquid Rb[3].

Equation (1) was inferred from data which Greenfield *et al.* only guarantee down to 0.3 Å^{-1} and their extrapolation down to $S(0)$ was done by "simply drawing a smooth curve through the data points," rendering the analysis of

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M-M somewhat suspect. Moreover it is at odds with the prediction made by other workers in the field[4,5], namely that $a_1 = 0$ and $a_3 \neq 0$, a coefficient related to the polarizability of the ions.

However, the recent experimental data of Waseda[6], and my own analysis of data previously published by him[7], does provide circumstantial evidence in support of the linear term. Although in my own estimation the result is not proven I shall proceed as if the linear term is indeed present.

Waseda's results go down to 0.08 Å^{-1} and he fits them to a sixth order polynomial. Whereas the leading term in his fitting is linear, there are qualitative differences with the analysis of M-M which are illustrated in Figure 1 for liquid Na. Moreover, if we are to believe in Waseda's results, the

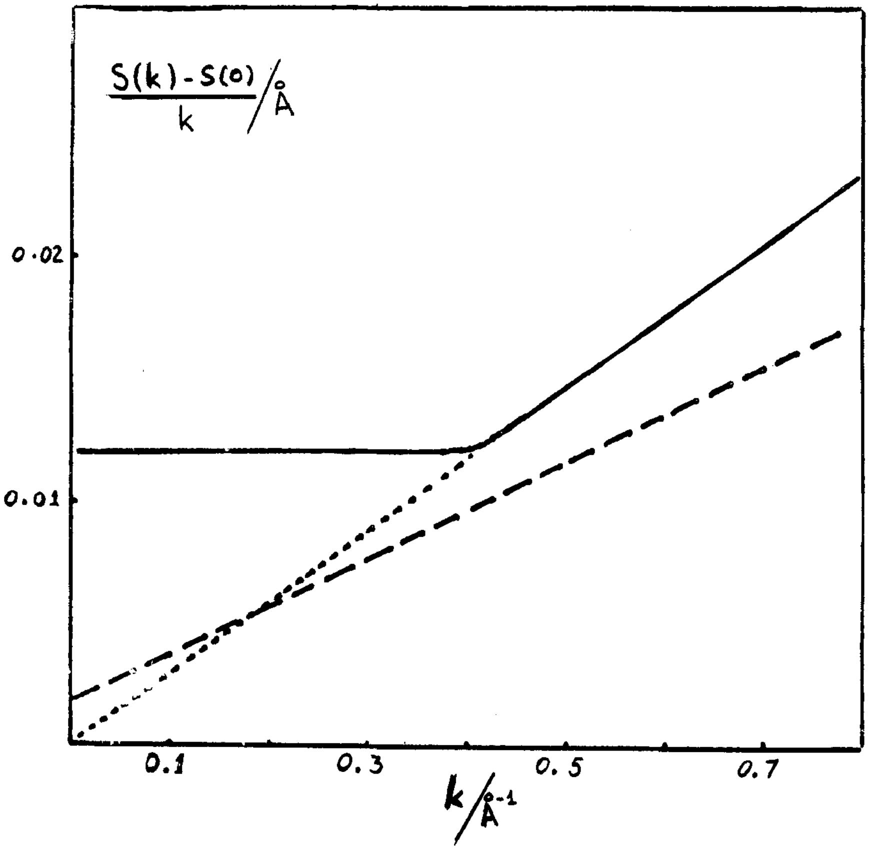

FIGURE 1 (S(k) – S(0))/k vs k for liquid Na:—— as deduced from the X-ray data of Waseda; ––– as deduced by Matthai and March from the X-ray data of Greenfield *et al.* Note that the extrapolation of the straight line (k 0.45 Å^{-1}) in Waseda's results intercepts the origin (shown by - - -)

fact that a_1 is negative for liquid Rb casts some doubts on the explanation given by M-M.

The purpose of this note is to advance an alternative explanation for the presence of a linear term in the small k-behaviour of $S(k)$ as obtained by X-ray scattering based on the assumption that liquid metals can be described as a binary mixture of electrons and ions. Such a description can be traced back to the work of Cowan and Kirkwood[8] (see also the interesting review by March[9]). In fact *all* the experimental evidence in support of the existence of a linear term is based on X-ray scattering. Admittedly the arguments presented below are of a qualitative nature, but I hope to quantify them in the near future.

Some years ago Egelstaff *et al.*[10] concluded that an analysis of scattering data revealed systematic differences at the first peak of $S(k)$—the point of reference they took throughout their work—when comparing X-ray and neutron scattering data in liquid metals. Their explanation was based on the fact that whereas neutrons—being scattered by nuclei—directly determine the ionic structure factor, X-rays—which are scattered by electrons—requires the liquid metal to be treated as a two-component system of conduction electrons and positive ions in order to carry out a proper analysis of the data. The possibility of extracting information on electron correlations in liquid metals by combining the above together with electron scattering data led to some important work of which the papers by Chihara,[11,12] Cusack *et al*,[13] Dobson[14] and Trigger[15] are probably a representative sample.

Following Dobson the total structure factor as obtained from X-ray scattering is written as

$$S_x(k) = \frac{f_i^2}{f_a^2} S_{i\text{-}i}(k) + \frac{f_e^2}{f_a^2} S_{e\text{-}e}(k) + 2\frac{f_i f_e}{f_a^2} S_{i\text{-}e}(k) \tag{2}$$

where the $S_{\alpha\beta}(k)$'s refer to the ion-ion (i-i), conduction electrons (e-e) and ion-conduction electrons (i-e) partial structure factors and the f_α's are the appropriate X-ray form factors, where the subscripts α refer to the species: i for ions, e for electrons and a for the (neutral) atom.

For simple liquid metals, where electron-ion coupling is weak and hence the interaction between electrons and ions can be represented by a pseudopotential with Fourier transform $v_{ps}(k)$, Trigger has shown that—in the adiabatic approximation—both $\mathrm{S}_{e\text{-}e}(k)$ and $S_{i\text{-}e}(k)$ may be written in terms of $S_{i\text{-}i}(k)$ and $\chi_e(k)$ the response function of a uniform electron gas, namely

$$S_{e\text{-}i}(k) = (Z)^{-1/2} v_{ps}(k)\chi_e(k) S_{i\text{-}i}(k) \tag{3}$$

and

$$S_{e\text{-}e}(k) = S^0_{e\text{-}e}(k) + (Z)^{-1}(v_{ps}(k)\chi_e(k))^2 S_{i\text{-}i}(k) \tag{4}$$

where Z is the valency and $S^0_{e\text{-}e}(k)$ is the structure factor of the electron fluid immersed in a uniform background of positive charge.

In (3) and (4) $S_{i\text{-}i}(k)$ is the structure factor resulting from using an effective interaction potential obtained from the pseudopotential $v_{ps}(k)$ and the response function $\chi_e(k)$. Hence, replacing (3) and (4) in (2), the total X-ray structure factor for a monovalent simple liquid metal is given by

$$S_x(k) = \frac{f_e^2}{f_a^2} S^0_{e\text{-}e}(k) + \frac{1}{f_a^2}(f_i + f_e v_{ps}(k)\chi_e(k))^2 S_{i\text{-}i}(k) \tag{5}$$

Following Eq. (5) a few remarks are in order.

First, both the studies of Evans and Sluckin and McLaughlin and Young are based on assuming a given effective interionic potential from which the small k-behaviour is studied within a given approximation. Irrespective of the approximation used it appears that the leading term in the neighbourhood of $k = 0$ is $0(k^2)$. It follows from equation (5) that this is only a measure of $S_{i\text{-}i}(k)$, and I assume henceforth that the small k-behaviour of

$$S_{i\text{-}i}(k) - S(0) \simeq 0(k^2),$$

a result which ought to be obtained from neutron scattering data. In other words only neutron scattering data—at small values of k—provides useful information about the long-ranged part of the effective interionic forces. Unfortunately, to my knowledge, there is practically no such data available in the literature.

Second, it is normal practice to model the form factors using relations of the type[16] $f_\alpha \simeq A_\alpha \exp(-B_\alpha k^2) + c_\alpha$, which at small k gives $f_\alpha \sim$ constant + $O(k^2)$. Moreover, bearing in mind the simplest type of expressions for $v_{ps}(k)$ and $\chi_e(k)$ available in the literature, the above together with the remarks concerning the small k-behaviour of $S_{ii}(k)$, rules out the possibility that the second term on the rhs of equation (5) contributes with a linear term to $S_X(k)$. In fact only $S_{e\text{-}e}(k)$ is capable of yielding, at small k, a leading term of $0(k)$. Indeed it is well known that in the Hartree-Fock approximation,[17] with k_F denoting Fermi's wave number,

$$\begin{aligned} S_{e\text{-}e}(k) &= \frac{3}{4}\frac{k}{k_F} - \frac{1}{16}\left(\frac{k}{k_F}\right)^3 \quad 0 < k \leq 2k_F \\ &= 0 \qquad\qquad\qquad\qquad \text{otherwise} \end{aligned} \tag{6}$$

Although Eq. (6) is too simplistic ignoring, as it does, the effects of exchange and correlation, it is enough for the purposes of arguing that it is $S^0_{e\text{-}e}(k)$ which dominates the small k-behaviour of the structure factor of liquid metals when obtained from X-ray scattering data. Of course a proper theory, geared towards obtaining quantitative results, should go beyond Eq. (6). Moreover, in those cases when the electron-ion coupling cannot be assumed to be weak the formalism used herein breaks down and a new approach is required.

Third, a few comments on the experimental results are in order. The X-ray data obtained by Waseda—or, more precisely, the polynomial fit chosen—lead, in my view, to some erratic behaviour in the signs of the coefficients a_1 and a_2 which are the source of the somewhat sceptical view expressed at the beginning of this note. More experimental results are required so as to have a clearer view of trends in the behaviour of $S_X(k)$. Also, it is hoped that neutron scattering data becomes available in the near future. It follows from the preceeding discussion that the largest differences between X-ray and neutron scattering should be observed at small values of k; a result which, in my view, is already implied in the works of Chihara and Trigger.

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