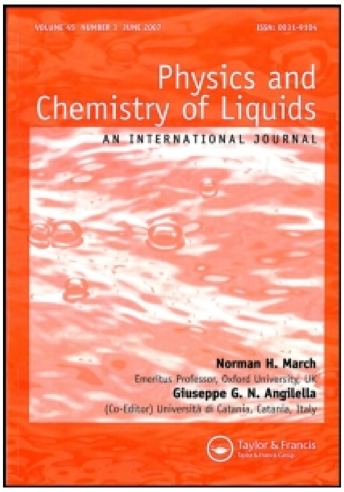

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Is there a Linear Term in the X-ray or Neutron Scattering in a Liquid Metal at Small Wave Number?

N. H. March[a]; M. Silbert[bc]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England [b] Department of Physics, Ben Gurion University of the Negev, Beer, Sheva, Israel [c] School of Mathematics and Physics University of East Anglia, Norwich, UK

To cite this Article March, N. H. and Silbert, M.(1983) 'Is there a Linear Term in the X-ray or Neutron Scattering in a Liquid Metal at Small Wave Number?', Physics and Chemistry of Liquids, 13: 2, 155 — 157
To link to this Article: DOI: 10.1080/00319108308080773
URL: http://dx.doi.org/10.1080/00319108308080773

Phys. Chem. Liq., 1983, Vol. 13, pp. 155–157
0031-9104/83/1302-0155$18.50/0

Letter

Is there a Linear Term in the X-ray or Neutron Scattering in a Liquid Metal at Small Wave Number?

N. H. MARCH

Theoretical Chemistry Department, University of Oxford, 1 South Parks Rd, Oxford OX1 3TG, England.

and

M. SILBERT†

Department of Physics, Ben Gurion University of the Negev, POB 653, Beer Sheva 84105, Israel.

(*Received May 16, 1983*)

We examine further, on theoretical grounds, whether a k term, in the small angle X-ray structure factor of liquid simple metals, has a well established theoretical basis. It is first pointed out that, whereas in the ion-ion structure factor it appears that the collective behaviour introduces a k term, in the electron-electron structure factor collective plasmon behaviour appears to wipe out the k term of the non-interacting Fermi hole. We also emphasize the need of small angle neutron scattering data to probe directly the phonon mode.

Matthai and March[1] (subsequently referred to as M–M) have recently inferred, by analyzing the X-ray scattering data of Greenfield *et al.*,[2] that the measured small angle scattering leads one to an expansion of the small k ionic(nuclear) structure factor $S_{ii}(k)$ as

$$S_{ii}(k) = S_{ii}(0) + a_1 k + a_2 k^2 + a_3 k^3 + \cdots \tag{1}$$

M–M has proposed an explanation of the above behaviour, which has been pointed out by one of us (MS)[3] to be at variance with the prediction made

† On study leave from the School of Mathematics and Physics, University of East Anglia, Norwich, UK.

by other workers in the field,[4,5] who claim that $a_1 = 0, a_3 \neq 0$, whereas M–M find $a_1 = 0$, $a_3 \doteqdot 0$ from their work.

Because the measurements to date, at the relevant small angle we are concerned with here, are all made using X-rays,[2,6] one of us (MS[3]) has pointed out that the fact that the electron-ion liquids Na and K are two-component systems should be taken into account in discussing the X-ray data, the argument that neutron and X-ray scattering give different results going back to Egelstaff *et al.*[7]

Using an expression given by Trigger,[8] it is possible to express the total X-ray structure factor for a monovalent metal simple liquid as

$$S_x(k) = \frac{f_e^2}{f_a^2} S_{ee}^0(k) + \frac{1}{f_a^2} [f_i + f_e v_{ps}(k)\chi_e(k)]^2 S_{ii}(k) \tag{2}$$

where $S_{ee}^0(k)$ and $\chi_e(k)$ are, respectively, the electron–electron structure factor and the response function of a uniform electron fluid (jellium), while $v_{ps}(k)$ is the pseudopotential and the f_α's are the appropriate X-ray form factors. MS has then argued that, in principle, the X-ray structure factor could have a linear term from either the term involving $S_{ee}^0(k)$ or from the ionic structure term $S_{ii}(k)$. Accepting the predictions of Refs. 4 and 5, he has therefore argued that the linear k behaviour, if it is substantiated by further, more accurate and smaller angle measurements, comes from $S_{ee}^0(k)$ whereas M–M have assumed it comes entirely from $S_{ii}(k)$.

The purpose of the present note is to add two further points which were not stressed by M–M[1] or by MS[3]. The first point is that it is obviously now of considerable importance to have very accurate small angle scattering using neutrons, from potassium say, in order to compare these results directly with the X-ray data. Quite evidently, this is the key experiment that is missing to date, in order to resolve the point of difference in Refs. 1 and 3.

The second point we wish to emphasize is that the k term cited in Ref. 3 came from the Fermi hole approximation to $S_{ee}^0(k)$, namely, with k_F the Fermi wave number

$$S_{ee}^{\text{Fermi hole}}(k) = \frac{3}{4}\frac{k}{k_F} - \frac{1}{16}\left(\frac{k}{k_F}\right)^3 \qquad 0 \le k \le 2k_F$$
$$= 1 \text{ otherwise} \tag{3}$$

and of course exists in the absence of electron correlation. However, one of us, (NHM)[9] using the correlated ground state function of Gaskell[10] for jellium, has demonstrated that the plasmon exactly cancels the k term in the Fermi hole result (3), leaving the form[11] at small k as

$$S_{ee}^{\text{jellium}}(k) = \frac{\frac{1}{2}\hbar\omega_p}{4\pi\rho e^2} k^2 + \cdots \tag{4}$$

where ω_p is the usual plasma frequency $(4\pi\rho e^2/m)^{1/2}$. This is a satisfactory result from the standpoint of liquid structure theory, in that, if we define the Ornstein–Zernike direct correlation function $c(r)$ in the usual way from the jellium pair function $g_{ee}(r)$, which is essentially the Fourier transform of $S_{ee}(k)$, then the inclusion of the plasmon gives asymptotically

$$c(r) = \frac{-e^2}{\frac{1}{2}\hbar\omega_p r} \tag{5}$$

showing that, in the completely degenerate limit, the widely accepted result in classical liquids that $c(r)$ behaves asymptotically as $-\phi(r)/k_B T$, with $\phi(r)$ the pair potential again holds, provided the thermal energy $k_B T$ of classical theory is replaced by the zero-point energy $\frac{1}{2}\hbar\omega_p$ of the plasmon.

It seems to us an interesting theoretical point that, whereas in $S_{ii}(k)$, according to the arguments of M–M, the collective behaviour introduces a k term, in the electron–electron structure factor, collective plasmon behaviour cancels the k term of the non-interacting Fermi hole form.

On the strength of the preceding discussion it appears that, unless the electron–ion interaction has unexpectedly large effects, which we do not think are likely in Na and K, the presence of a linear term can only be associated with the collective motions of the ions.

But we reiterate, in spite of the theoretical arguments presented here, which inevitably all involve some degree of approximation, the decisive way to proceed is to have small angle neutron data to compare with the X-ray data.

Acknowledgements

One of us (MS) gratefully acknowledges the financial support from the Royal Society.

References

1. C. C. Matthai and N. H. March. *Phys. Chem. Liquids*, **11**, 207 (1982).
2. A. J. Greenfield, J. Wellendorf, and N. Wiser, *Phys. Rev.*, **A4**, 1607 (1981).
3. M. Silbert, *Phys. Chem. Liquids*, in the press.
4. R. Evans and T. J. Sluckin, *J. Phys. C*, **14**, 3137 (1981).
5. I. L. McLaughlin and W. H. Young, *J. Phys. F*, **12**, 245 (1982).
6. Y. Waseda, *Z. Naturforschung* (to be published).
7. P. A. Egelstaff, N. H. March, and N. C. McGill, *Can. J. Phys.*, **52**, 1651 (1974).
8. S. A. Trigger, *Phys. Lett.*, **A56**, 325 (1976).
9. N. H. March, Mathematical methods in solid state and superfluid theory, *SUSS Proceedings*, Eds. R. C. Clark and G. H. Derrick (Oliver and Boyd, Edinburgh), 1967.
10. T. Gaskell, *Proc. Phys. Soc.*, **80**, 1091 (1962).
11. N. H. March and M. P. Tosi, *Atomic Dynamics in Liquids*, (Macmillan: London), 1976.