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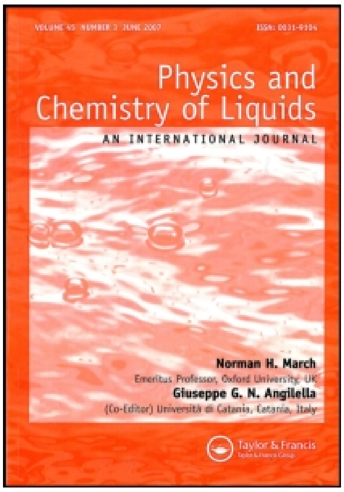

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N. H. March[a]
[a] Theoretical Chemistry Department, University of Oxford, Oxford, England

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Review Article

Small Angle Scattering from Liquids

N. H. MARCH

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

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A short review is given of the current interests in small angle scattering from liquids; condensed rare gases, liquid metals and molten salts being considered in turn.

1 INTRODUCTION

Though the theory of the small angle scattering of X-rays or neutrons from a simple liquid like argon was laid down almost two decades ago,[1] it is only fairly recently that it has been brought into direct contact with experiment.[2] In the course of doing this, Matthai and March were concerned to compare the results for liquid metals, such as Na and K, for which X-ray structure data are available,[3] with those for liquid argon. This has led to some controversy, but points the way to some further experiments which are needed. In addition to condensed rare gases, and liquid alkali metals, we shall briefly review results on molten salts, following the work of Rovere *et al.*[4]

2 SIMPLE MONATOMIC LIQUIDS LIKE ARGON

As shown in Ref. 1, the precise theory of the small angle scattering from, say, liquid argon, can be expressed through the small k expansion of the liquid structure factor $S(k)$:

$$S(k) = S(0) + a_2k^2 + a_3k^3 + \dots\dots \tag{2.1}$$

The theory of a_3 is readily given from the result that the Ornstein–Zernike direct correlation function $c(r)$ has the asymptotic form $-\phi(r)/k_BT$ at large

r and far from the critical point, where $\phi(r)$ is the pair interaction. If we neglect retardation effects, then $\phi(r) \sim -c_6/r^6$ at large r for a liquid like argon, where c_6 is the usual van der Waals constant, and we readily find for a_3 in eqn (2.1) the result

$$a_3 = \frac{\pi^2 \rho \{S(0)\}^2 c_6}{12 k_B T} \tag{2.2}$$

where ρ is the number density, while $S(0)$ is determined by fluctuation theory as

$$S(0) = \rho k_B T\, K_T, \tag{2.3}$$

K_T being the isothermal compressibility.

In Figure 1 of Ref. 2, Matthai and March have plotted the measured small-angle scattering from the data of Yarnell *et al.*[5] in the form suggested by Eqn. (2.1), $[S(k) - S(0)]/k^2$ vs k. Though it is true that Yarnell *et al.* had to extrapolate their measured diffraction data to join on to the compressibility data for $S(0)$ in Eqn. (2.3), the estimated value of a_3 (0.35 Å^3) agrees well with the theory estimate from Eqn. (2.2) of 0.375 Å.[3] As Robinson and March[6] have shown, the constant c_6 in liquid argon is expected to be reduced from its free space value by some few percent only, due to the van der Waals interactions occurring in the condensed dielectric medium.

As for a_2, Woodhead-Galloway *et al.*[7] have estimated the coefficient for various thermodynamic states. Though they used both virial expansion and random phase approximation techniques, the latter is much more basic than the density expansion at high density. The coefficient of k^2 in Eqn (2.1) has been calculated for liquid argon and the detailed results are given in Figures 4 to 6 of Ref. 7. Comparison with the virial expansion over a density range for which that is valid is found to be good. Matthai and March estimate $a_2 = -0.08$ Å^2 from theory, and -0.12 Å^2 from experiment. The hard sphere Percus-Yevick results are also calculated by Woodhead-Galloway *et al.* and their work shows that even the sign of the k^2 term is usually wrongly given by a hard sphere theory. In this context, we must refer here to some very recent comments by Haymet[8] in the course of a discussion of the freezing of hard spheres. We quote Haymet's comments "... note that the small k dependence of the liquid structure factor is not well known, even for simple substances. The term linear in k must vanish, by rotational invariance but the sign of the term quadratic in k is controversial". The above discussion, and in particular the comparison with experiment of the predictions of Eqns. (2.1) and (2.2) with the experiments of Yarnell *et al.*, shows that Haymet is being overly pessimistic in these comments, misled perhaps by the hard sphere model. We will return to his comment about the term linear in k in the following section.

3 LIQUID ALKALI METALS

We turn then, from the rather clearcut situation in the condensed rare gases, to the more controversial field of simple liquid metals. The following discussion is based on the work of Matthai and March,[2] plus reference to the later contributions of Silbert[9] and of March and Silbert.[10]

Essentially, Matthai and March set out to examine whether there was evidence for van der Waals interactions in liquid metals, in the light of the work on the theory of such interactions detailed in Ref. 2. But when one used an expansion of the form (2.1) above, no agreement with the diffraction data of Greenfield *et al.*[3] could be obtained. They[2] therefore proposed a theory based on the model of independent density fluctuations, which is supported by thermal properties of the simple liquid metals, as well as the direct neutron observation of a collective mode in liquid *Rb* by Copley and Rowe.[11] They[2] wrote, following the method of Feynman for He^4, the dispersion relation $\omega(k)$ of the collective mode of the liquid metal in terms of the structure factor $S(k)$ as

$$\omega^2(k) = \frac{k^2 k_B T}{M S(k)} \tag{3.1}$$

with M the atomic mass. If now the collective mode is taken to have the small k form

$$\omega(k) = v_s k + dk^2 + \dots. \tag{3.2}$$

then the dispersion of the collective mode leads to a linear term in k at small k in the liquid metal. Here, it is necessary to refute the further assertion of Haymet,[8] referred to in Section 2, that a linear term in k is excluded by rotational invariance. This would exclude the well established Feynman result in liquid He^4 at $T = 0$ that $S(k) = \hbar k/2Mv_s$, with v_s again the velocity of sound.

When Matthai and March considered the expansion suggested by the above collective mode theory in the light of the experiments of Greenfield *et al.*, namely

$$S(k) = S(0) + a_1 k + a_2 k^2 + a_3 k^3 + \dots \tag{3.3}$$

the data can be fitted rather naturally by suitable choice of a_1, and a_3 is then found to be approximately zero, in accord with arguments that the van der Waals interaction will be screened out in the liquid metal.

However, in later work, Silbert[9] has argued that the fact that the liquid metal is a two-component liquid is important. According to his arguments, the X-ray and neutron small angle scattering will be different (see, however March and Silbert[10]).

It is clearly of considerable interest now to have neutron scattering data at very small angles to compare and contrast with the X-ray measurements of Greenfield *et al.*, which were the basis of the Matthai-March analysis.

4 MOLTEN SALTS

Rovere *et al.*[4] have considered the partial structure factors S_{++}, S_{+-} and S_{--} in molten salts at small wave numbers. In addition to a term of order k^3 arising in the small k expansion of these S_{ij}'s at small k from the presence of van der Waals dipole-dipole interactions, as discussed above in section 2, these workers show that the term of order k^2 in $S_{++} - S_{--}$ is determined by the difference in partial molar volumes of the two ionic species. Furthermore, the charge-charge structure factor, $S_{++} + S_{--} - 2S_{+-}$, is determined at order k^4 by the screening length of the system.

All the relevant coefficients in the various expansions of the S_{ij}'s and the partial direct correlation functions c_{ij}'s, are evaluated by Rovere *et al.* for a charged hard sphere model of the family of molten alkali halides in the mean spherical approximation, using input parameters adjusted to account for the isothermal compressibility near freezing. These workers also estimate the magnitude of the van der Waals term.

To illustrate their results, we take one of their examples, of RbCl at 988K, where, with k in Å^{-1} they find for the charge-charge structure factor $S_{QQ}(k)$ the small k expansion

$$S_{QQ}(k) = 0.046k^2 + 0.058k^4 + 0(k^5) \tag{4.1}$$

while the number-charge structure factor $S_{NQ}(k)$ is found to have the form

$$S_{NQ}(k) = -0.0003k^2 + 0(k^4). \tag{4.2}$$

Finally the number-number partial structure factor is predicted as

$$S_{NN}(k) = 0.120 + 0.074k^2 + 0.166k^3 + 0(k^4). \tag{4.3}$$

It would be of obvious interest to compare these results with small angle neutron scattering experiments, but we are not aware of such data at the time of writing.

There is a further reason for the interest in the small angle scattering from ionic melts. This stems from the work that has been carried out recently on the theory of freezing of $BaCl_2$ into a fast ion conducting phase. Following the theory worked out by March and Tosi[12] to deal with a situation in which the freezing of $BaCl_2$ specifically is regarded as driven by the marked cation ordering in the liquid, d'Aguanno *et al.*[13] have made a fully quantitative application of the freezing theory to this material. Their findings show that there is now considerable interest in the partial molar volumes in $BaCl_2$. They draw the conclusion that in molten $BaCl_2$ there is some phenomenon akin to classical Wigner crystallization occurring in the cation assembly, a 'classical Coulomb hole' existing due to strong repulsions between the divalent ions. Though the partial molar volumes are, of course, well defined thermodynamically, there appears presently no other way to extract them from experiment than through small angle scattering measurements.

5 SUMMARY

For condensed rare gases, the theory of small angle scattering appears to be satisfactory in relation to the experiments of Yarnell *et al.* on liquid argon.[5] Even here, it would be valuable to have further experiments which went down to smaller values of k and thereby avoided the neccesity of interpolation between the diffraction measurements and the limiting value of the structure factor in the long wavelength limit, as determined by the isothermal compressibility. Also, test of the variation of the small angle scattering with fluid density would be worthwhile.

When one turns to liquid metals, the situation is less clear. However, the simple theory used for liquid argon no longer works, and it appears that collective effects are playing a role. Presently, it is of importance to clarify whether the small angle scattering from the liquid alkalis is importantly different for X-rays compared with neutrons and therefore small angle data for neutrons would be most welcome to test some of the current ideas.

Finally, there are theoretical predictions for the molten alkali halides, and in particular we have summarized above the results of Rovere *et al.* for molten RbCl. Small angle scattering data on this material should be a feasible project. However, from a different line of argument, namely current advances in the theory of freezing of $BaCl_2$ into a fast ion conducting phase, the interest in extracting in this material the difference in the partial molar volumes from small angle scattering experiments is stressed.

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