The Partial Structure Factor of Sulphur in Liquid CS_2 by Combining X-ray and Neutron Diffraction Results

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The partial structure factor for sulphur in liquid CS_2 at 20 °C has been computed by combining published x-ray and neutron diffraction results. Assuming that there are no correlations of molecular orientations, it is found that the main peak height of this sulphur-sulphur partial structure factor is smaller than that for carbon-carbon. This result is discussed in relation to the solid state structure and recent theoretical calculations.

1. Introduction

The solid state crystal structure of CS_2 is tetragonal[1] and a feature of the structure is that only sulphur atoms are in near neighbour contact. At -115.7 °C the crystal melts with a large entropy of melting which has been taken to indicate[2] that molecules have free rotation in the liquid. This is confirmed by low entropy of vapourization[3] and the well known D. C. Kerr effect, though it has been stated[4] that the Kerr constant is 40% lower than would be expected from completely free movement. In order to study the structure of the liquid diffraction measurements have been made by a number of workers. The first were made by Krogh-Moe[3], followed by Street[5] who used a diffractometer specially designed for work on high vapour pressure liquids[6]. In both cases these x-ray data were Fourier transformed to give a so-called electronic distribution function. Unfortunatly there are fundamental physical objections to such a procedure which have been discussed in detail by Page and Powles[7]. Most recent measurements are those of Suzuki and Egelstaff[8], employing neutron diffraction, and Sandler and Narten[9], using x-ray diffraction. Suzuki and Egelstaff[8] have interpreted their results using a very careful description of neutron diffraction from molecular liquids due to Egelstaff, Page and Powles[10]. This approach shows how, by the use of models, a study can be made of possible correlations of molecular orientations. Sandler and Narten[9] interpret their x-ray diffraction results in a similar way, but also use Fourier transformation of their diffraction results. In order to avoid the use of either of the procedures given above and obtain complete information about liquid CS_2, at least three scattering experiments[11] would have to be carried out to obtain the partial structure factors $S_{C-C}(K)$, $S_{S-S}(K)$ and $S_{C-S}(K)$ (where K is the modulus of the scattering vector for x-rays). One method of achieving such a result is to make diffraction measurements using three different types of radiation which are scattered differently by the atoms of the molecule. In the present case measurements with only two radiations are available but fortunatly the relative scattering powers of C and S are very different. The ratio of the scattering lengths of C to S is 2.34 for neutrons and 0.374 for x-rays. It can be assumed that carbon is at the centre of the molecule, so neutron diffraction measurements give information about the distribution of molecular centres, which is identical to the partial structure factor $S_{C-C}(K)$. The largest contribution to x-ray diffraction measurements will clearly come from sulphur atoms, thus provided an adequate assumption can be made about $S_{C-S}(K)$, and using $S_{C-C}(K)$ from neutron measurements, x-ray results should yield $S_{S-S}(K)$.

2. Theory

Egelstaff et al.[10] have discussed neutron diffraction from molecular liquids and have shown that it is useful to calculate a molecular structure factor $S_m(Q)$ (where Q is the modulus of the scattering vector for neutrons). The feature of this structure factor is that it can be reduced to three components and each plays a physically recognisable role in the structure of the liquid.

$$S_m(Q) = F_1(Q) + F_2(Q)\,[S_c(Q) - 1] \qquad (1)$$

where $F_1(Q)$ = molecular form factor, $F_2(Q)$ = molecular correlation from factor, $S_c(Q)$ = molec-

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ular centre structure factor. Page and Powles[7] have made certain approximations and obtained an equivalent structure factor, $S_m(K)$, which can be expressed in a form similar to Eq. (1), but calculated from x-ray results, using the following expressions for $F_1(K)$ and $F_2(K)$.

$$\begin{aligned} F_1(K) = {} & [f_C(K) + 2 f_S(K)]^{-2}\, [f_C^2(K) + 2 f_S^2(K) \\ & + 4 f_C(K) f_S(K)\, (\sin K r_{C-S})/K r_{C-S} \\ & + 2 f_S^2(K)\, (\sin K r_{S-S})/K r_{S-S}] \end{aligned} \tag{2}$$

where $f_C(K)$ is the atomic scattering factor for C and r_{C-S} is the interatomic distance between carbon and sulphur in the molecule. Assuming that there are no correlations of molecular orientations, it has been shown[8] that $F_2(K)$ may be written as;

$$\begin{aligned} F_2(K) = {} & [f_C(K) + 2 f_S(K)]^{-2} \\ & \cdot [f_C(K) + 2 f_S(K)\, (\sin K r_{C-S})/K r_{C-S}]^2 . \end{aligned} \tag{3}$$

On the basis of equations similar to Eqs. (2) and (3), Suzuki and Egelstaff[8] have calculated the molecular centre structure factor, $S_c(Q)$. It is reasonable to assume that this is identical to the partial structure factor, $S_{C-C}(K)$ and, moreover, will be obtained with reasonable accuracy since C, the central atom of the molecule, scatters neutrons more strongly than does sulphur. In the x-ray case $S_m(K)$ will contain the largest contribution from the sulphur atoms, thus with $S_{C-S}(K)$ given by the terms involving C – S interactions from $F_1(K)$ and $F_2(K)$, given above, the partial structure factor $S_{S-S}(K)$ may be written as;

$$\begin{aligned} S_{S-S}(K) = {} & S_m(K)\, [f_C(K) + 2 f_S(K)]^2 / \, 2 f_S^2(K) \\ & - S_c(Q)\, \{f_C^2(K)/2 f_S^2(K) + [2 f_C(K)/f_S(K)] \\ & \cdot (\sin K r_{C-S})/K r_{C-S}\} . \end{aligned} \tag{4}$$

In evaluating Eq. (4), $S_m(K)$ was calculated[7] using the data of Street[5] and the analytic form of the atomic scattering factors[12]. $S_c(Q)$ was computed from tabulated data for $S_m(Q)$ given in [8] using Eq. (1) and the neutron equivalents of Eqs. (2) and (3), together with $r_{C-S} = 1.554$ Å, b_S, the neutron scattering lengths for sulphur $= 0.663 \times 10^{-12}$ cm, $b_C = 0.285 \times 10^{-12}$ cm.

3. Discussion of Results

Figure 1 shows the three molecular structure factors for CS_2 obtained from [5, 8, 9]. As would be expected from the difference in the relative scattering powers of carbon and sulphur, the first main peaks of $S_m(Q)$ and $S_m(K)$ are found at different values of the scattering vector. It should also be noted that the recent results of Sandler and Narten[9] give an $S_m(K)$ which is larger than the $S_m(K)$ obtained by Street[5] and outside the error band of ±7%. However, the peaks and troughs are in good agreement, even at large values of K.

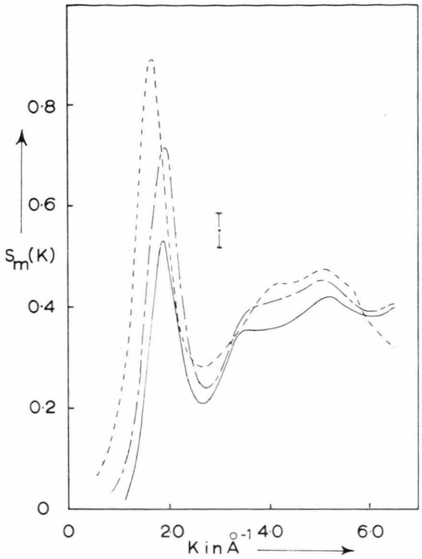

Fig. 1. Molecular structure factors for CS_2: ——— $S_m(K)$ from the data of Street[5]; — — — $S_m(Q)$, Suzuki and Egelstaff[8]; - ——— - $S_m(K)$, from the data of Sandler and Narten[9]; Ⲓ Error bars.

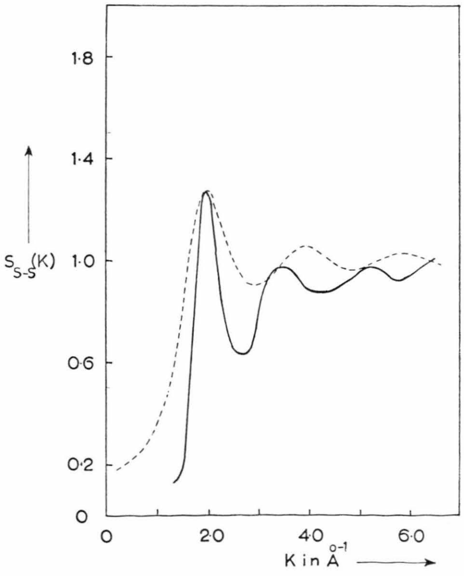

Fig. 2. Partial structure factor for sulphur: ——— $S_{S-S}(K)$ obtained from the present work; — — — Hard sphere curve, $\eta = 0.21$, hard sphere diameter = 3.19 Å.

Figure 2 shows $S_{S-S}(K)$ compared with a hard sphere structure factor[13] which has the same first peak height and corresponds to a packing density η of 0.21. Suzuki and Egelstaff[8] have compared their $S_c(Q)$, and hence $S_{C-C}(K)$, with these hard sphere structure factors and find best agreement with $\eta = 0.36$. These values of η are important because they enable the present results to be compared with real space models, without Fourier transforming $S_{S-S}(K)$ and $S_{C-C}(K)$ to give partial distribution functions $g_{S-S}(r)$ and $g_{C-C}(r)$. Fourier transformation was not justified because of the low accuracy of the partial structure factors. However, from the packing densities given above, a deduction was made about the relative heights of the main peaks of the partial distribution functions, e.g. $g_{S-S}(\max)$. From the present work it was found that $\eta_{C-C} > \eta_{S-S}$ and from a knowledge of the behaviour of hard sphere liquids[13] it was deduced that $g_{C-C}(\max) > g_{S-S}(\max)$. This was very different from the solid state structure[1], mentioned in the Introduction, where only sulphur atoms were in contact. If the same tendency were present in the liquid it would be expected that $g_{C-C}(\max) < g_{S-S}(\max)$. However, since all experiments were carried out at 20 °C which was a very much higher temperature than the melting point of -115.7 °C, it was possible that the preference for sulphur atoms to be in contact was destroyed. A larger value for $g_{S-S}(\max)$ than $g_{C-C}(\max)$ was found by Lowden and Chandler[14] as a result of their theoretical calculations using the reference-site-interaction model. However, one of the assumptions that was used in this model was that liquid structure was determined by only size and shape of molecules and no multipole moments were considered. CS_2 has a quadrupole moment of 1.8×10^{-26} esu cm^2, which could influence correlations of molecular orientations, possibly bringing carbon atoms closer together. Sandler and Narten[9], in spite of objections to the procedure[7], Fourier transformed their molecular structure to give a total distribution function. This experimental function was in reasonable agreement with the theoretical total distribution function[14]. It was inferred that their results[9] supported $g_{C-C}(\max) < g_{S-S}(\max)$.

Finally, it must be pointed out that the present $S_{S-S}(K)$ has been calculated on the assumption of no correlations of molecular orientations. Clearly it would be possible to recalculated this partial structure factor using other assumptions. This was not done because of the large errors in the experimental data, $\pm 10\%$ in $S_m(Q)$ and $\pm 7\%$ in $S_m(K)$. Further calculations must await better experimental results, but the present note indicates the usefulness of carrying out both x-ray and neutron diffraction measurements on liquid CS_2.

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