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1990 J. Phys.: Condens. Matter 2 8427

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The structural properties of liquid sulphur

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Received 15 December 1989, in final form 9 August 1990

Abstract. Neutron diffraction experiments over the momentum transfer range $0 < Q < 40 \text{ \AA}^{-1}$, have been used to investigate the properties of liquid sulphur from 131 °C to 230 °C, i.e. at conditions around the λ -transition ($T_\lambda = 159 \text{ °C}$). The data have been transformed to give an accurate pair correlation function from which the absolute numbers of atoms in given molecular configurations may be determined. These data seem to be inconsistent with the picture of 'crown'-shaped S_8 molecules below T_λ . Also it has been found that the diffraction pattern may be analysed as though the liquid was an assembly of roughly spherical molecular units. In this case each unit would contain about six atoms, and the λ -transition could be related to the percolation limit for the units. It is concluded that a fundamental diffraction analysis of the states of sulphur has thrown new light on long-standing problems.

1. Introduction

The study of elemental sulphur offers an attractive challenge because of the unique diversity of stable molecules that it can form in the gaseous, liquid and solid state and because the chemical conversions of molecular species occur at moderate temperature conditions [1–4].

The stable crystalline modification at room temperature is orthorhombic sulphur (S_α). It is believed to consist of S_8 -rings as structural units with an average bond length and angle of 2.05 Å and 108°, respectively [4]. It melts at about 115 °C and forms a light yellow liquid of relatively low viscosity. According to an interpretation of IR and Raman experiments [5, 6], this liquid is made up mainly of S_8 ring molecules, too. Above the 'critical temperature' of 159 °C, the viscosity rises drastically and also other physical properties such as the refractive index, density, thermal expansion and specific heat show characteristic anomalies at this so-called λ -transition [4–14]. It is generally believed, that these changes are due to the formation of long chain polymer components in the melt [1–4]. Evidence of polymeric sulphur S_μ and S_8 rings as main constituents in liquid sulphur for $T > 159 \text{ °C}$ comes mainly from IR, Raman and HPLC dissolution experiments [1, 6]. The relationship of these results to the true composition of the liquid is a matter of conjecture.

It has been observed, that if molten sulphur is heated above 159 °C, preferably to 200 °C–250 °C, and then rapidly quenched to a temperature around –30 °C, a translucent elastic substance is obtained (elastic sulphur). At even lower temperatures (e.g. –100 °C) it is a hard material, but on raising the temperature to above –30 °C it loses its elastic properties and hardens due to a process of crystallization [15]. It has been assumed, that elastic sulphur is a mixture of S₈ rings and of polymeric sulphur, both monomer and polymer being in an amorphous state, which crystallize at higher temperatures and then exhibit a distinct x-ray diffraction powder pattern [15–22].

The structure of sulphur in its liquid and quenched states has attracted considerable experimental [16–28] as well as theoretical [15, 29–36] attention for many decades. However, still no model accounts satisfactorily for all its properties. To obtain a better understanding of these systems a variety of diffraction experiments are needed [34] and, we believe, they would be very informative. In order to elucidate the structural characteristics of sulphur in its various phases, we have recently started a systematic investigation of sulphur by neutron diffraction, which should cover the quenched, non-crystalline and also the liquid sulphur state from the melting point up to its critical point ($T_c = 1040$ °C, $P_c = 203$ bar, $d_c = 0.58$ g cm⁻³ [37]).

In this paper we describe the first results on liquid sulphur for the temperature range of 131 °C–230 °C, i.e. around the λ -transition. For temperatures below this transition it has been assumed that the liquid is composed of S₈ units which have the ‘crown’ structure found in crystalline α -sulphur. One of the objectives of our work is to test this hypothesis, and also the corresponding hypothesis that above the λ -transition the local structure is preserved (although the longer range structure is believed to alter). We shall do this by exploiting our absolute measurements of intensities in r -space. Thus in this paper we explore the under-pinning of conventional ideas, and in this connection it is worth emphasizing the almost unique advantage of liquid diffraction measurements in providing absolute intensities. A preliminary study was published in [27].

2. Experimental method

Two series of diffraction experiments were carried out. The first series of neutron diffraction experiments were performed at the NRU reactor in Chalk River Nuclear Laboratories, using the GII diffractometer. The wavelength of the incident neutrons was $\lambda = 2.395$ Å and the range of momentum transfer covered $0.2 < Q/\text{Å}^{-1} < 4.4$. The neutron beam was 2 cm wide and 6 cm high. The sample was mounted in an argon environment to reduce the background scattering. The scattered neutrons were detected by 13 ³He counters set at various angles and mounted 2.2 m from the sample. Each counter was scanned in 0.5° steps and the total angular range covered was 3° to 115°. The sample container was an aluminium cylinder of 22 mm inner diameter with a wall thickness of 0.2 mm over the neutron beam height. The sample temperature was controlled by two automatically regulated resistance heating devices, mounted above and below the neutron beam window. With this instrument it was possible to perform measurements on the liquid sample at nine temperatures from 131 °C to 220 °C.

For the second series of experiments the LAD instrument of the ISIS accelerator at the Rutherford Appleton Laboratory was used. It is a time-of-flight instrument covering a momentum transfer range of $0.2 < Q/\text{Å}^{-1} < 50$ with good resolution. The wavelength range used was from 0.1 to 7 Å and the detectors were at fixed angles of 10°, 20°, 35°, 60°, 90° and 150°. Segments of the spectra from all angles were combined to produce the

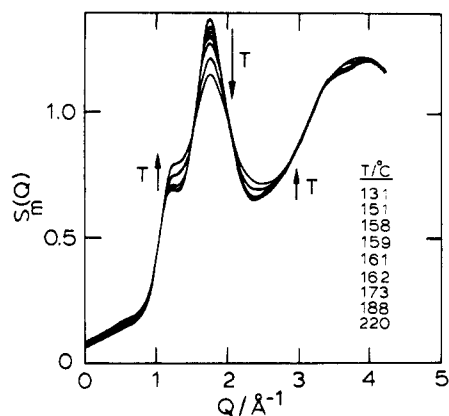


Figure 1. Experimental structure factor $S_m(Q)$ of liquid sulphur in the temperature range 131 °C–220 °C.

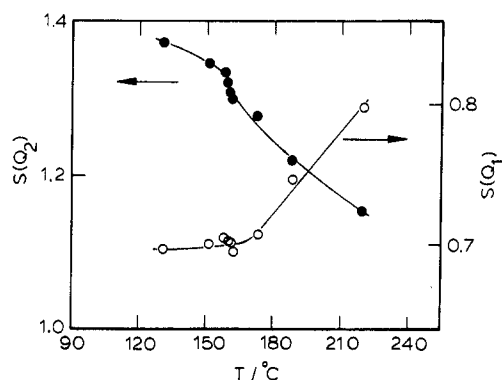


Figure 2. The maxima $S(Q_1)$ and $S(Q_2)$ of the first two peaks in $S_m(Q)$ of liquid sulphur as a function of temperature.

final $S(Q)$. The same liquid samples (except that a vanadium container was used in place of the aluminium one) were used for liquid temperatures of 150 °C and 230 °C only.

Details of the data evaluation are given elsewhere [38–40]. Briefly, the structure factor $S(Q)$ for the liquid samples was obtained from the measured scattering intensities by employing the usual corrections for background, absorption, multiple scattering and inelasticity. The differential scattering cross sections were normalized to an absolute scale by comparison of the sample's scattering intensity with that of a standard vanadium sample. For $Q < 0.2 \text{ \AA}^{-1}$ the structure factor was extrapolated to $S(0) = nk_B T \chi_T$ with the number density n and the isothermal compressibility χ_T taken from the literature data [7].

3. Experimental results

Figure 1 depicts the measured structure factor $S_m(Q)$ from the first series, for liquid sulphur at several temperatures from 131 °C to 220 °C. As can be clearly seen, the first maxima are composed of a shoulder at $Q_1 = 1.25 \text{ \AA}^{-1}$ and peaks at $Q_2 = 1.75 \text{ \AA}^{-1}$ and $Q_3 = 4.0 \text{ \AA}^{-1}$. Their positions remain essentially constant with increasing temperature, but the relative intensities $S(Q_1)$ and $S(Q_2)$ start to change around 160 °C (see figure 2), the temperature where the λ -transition occurs. For $T > 160 \text{ °C}$, $S(Q_1)$ and $S(Q_2)$ continue to change linearly with increasing temperature. It is obvious that the structural changes accompanying this transition are relatively small.

In order to extend our data to higher Q we employed the second series of experiments. Figure 3 shows the molecular structure factor $S_m(Q)$ of liquid sulphur at $T = 150 \text{ °C}$ and $T = 230 \text{ °C}$ measured up to $Q = 40 \text{ \AA}^{-1}$. We noted that little temperature dependence was seen at high Q . The data were then Fourier transformed to the radial distribution function $g(r)$. In figure 4 we show curves for the function $g(r)$, for the two liquid states at $T = 150 \text{ °C}$ and $T = 230 \text{ °C}$. Each of these curves shows about two nearest neighbours centred around 2.06 \AA and a second concentration of roughly 3 atoms at a distance of about 3.35 \AA (see table 1). Whereas the peaks at the first two distances are almost

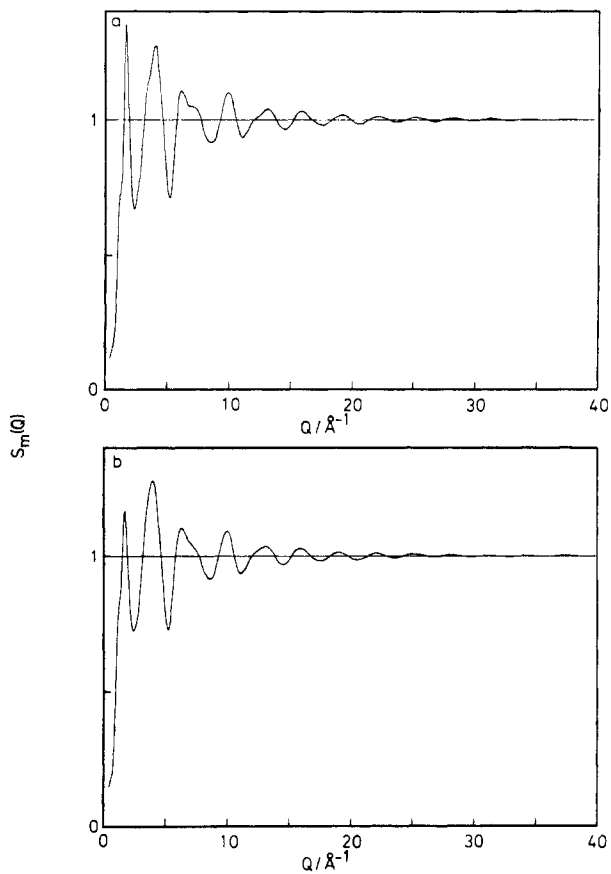


Figure 3. The molecular structure factor $S_m(Q)$ of liquid sulphur at (a) $T = 150\text{ }^\circ\text{C}$ and (b) $T = 230\text{ }^\circ\text{C}$.

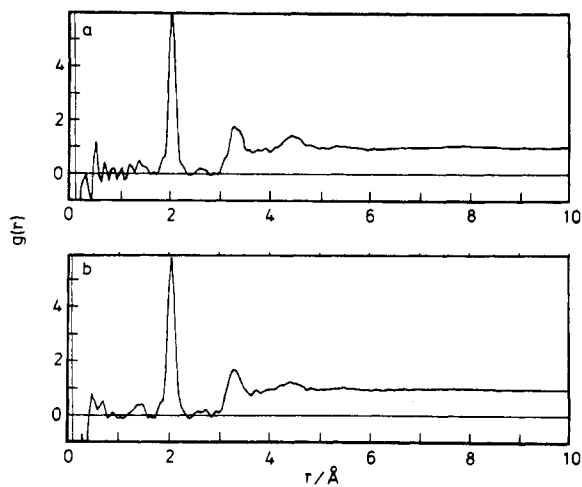


Figure 4. The pair distribution function $g(r)$ of liquid sulphur for temperatures of (a) $150\text{ }^\circ\text{C}$ and (b) $230\text{ }^\circ\text{C}$.

Table 1. Summary of lowest two peaks in $g(r)$ (labelled 1 and 2 in equation (2)).

Temperature, $T/^\circ\text{C}$	Peak position, r_1 or $r_2/\text{\AA}$	Peak area, A_1 or A_2^\dagger	Width parameter, $u/\text{\AA}$	
150	2.06 ± 0.01	1.8 ± 0.1	0.044 ± 0.001	Lowest peak (1)
230	2.06 ± 0.01	1.7 ± 0.1	0.047 ± 0.001	
150	3.35 ± 0.02	3.0 ± 0.1	0.10	Second-lowest peak (2)
230	3.35 ± 0.02	2.9 ± 0.1	0.11	

\dagger The areas A_1 and A_2 for either the ring or chain model should be $A_1 = 2.0$ and $A_2 \approx 2.2$ —where the extra 0.2 for A_2 arises from part of the area of the broad intermolecular component taken over the narrow range of this peak. The ratio A_1/A_2 is thus 1.1 compared to the experimental values of 1.7 ± 0.2 .

independent of temperature, the third peak for the liquid (see figure 4) around 4.45 \AA is broad and decreases with increasing temperature while the fourth peak at 5.3 \AA slightly increases with increasing temperature (see figure 6).

4. Discussion

There have been several attempts, to model liquid sulphur [25, 35, 36]. Models like S_8 rings and freely rotating chains or relaxational computer models including both contributions have been suggested for the regions below and above the λ -transition, respectively. For these models the first peak in the distribution function should contain 2 atoms of 2.06 \AA . The peak observed experimentally at $r_1 = 2.06 \text{ \AA}$ contains slightly less than two atoms within the sulphur molecule (see table 1). The intramolecular next nearest neighbour distance of S_8 rings [4] or of a freely rotating sulphur chain [41, 42] is 3.3 \AA and should contain two atoms and the intermolecular density at this distance should be small and distributed broadly. For example, using the known crystal structure of solid α - or β -sulphur [45, 46], the intermolecular intensity in $g(r)$ over the range 3.0 to 3.6 \AA may be calculated. In this way we estimated that for solid-like structures the total area in this range should be 2.25 rather than the 3.0 ± 0.1 observed (see table 1). The use of somewhat wider ranges was tried and the observed area increased faster than the calculated area. For example, the observed area extended to the first minimum in $g(r)$ (see figure 4—which would correspond to the usual definition of a coordination number), is 3.5 and the calculated area 2.75. These results may indicate that the conventional 'crown'-shaped molecule of S_8 as known from the solid state is not applicable to the liquid. It is possible that either deformed S_8 molecules of another shape occur, or that the molecule contains a different number of atoms.

The experimental data of figures 3 and 4 strongly suggest that a molecular type of model should be used in the analysis and also this view is not inconsistent with the usual ring or chain models. Accordingly we have written

$$S_m(Q) = f_1(Q) + S_D(Q) \quad (1)$$

where $f_1(Q)$ is the form factor for a pseudo-molecular unit and $S_D(Q)$ is due to interference scattering between molecular units. Molecular units may be expected to produce sharp peaks at low r in $g(r)$, which are fairly independent of temperature. Hence

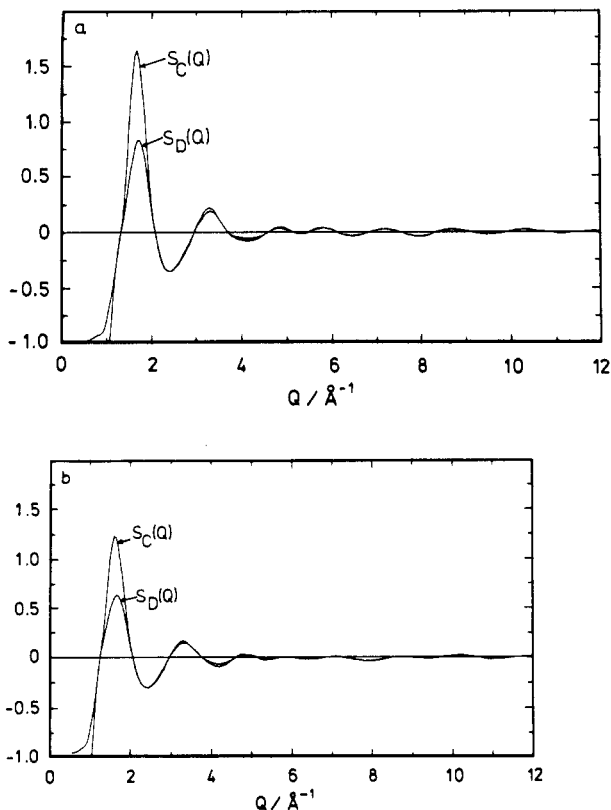


Figure 5. The structure factor $S_c(Q)$ (minus 1) from equation (4) compared to $S_D(Q)$ from equation (1). (a) $T = 150\text{ }^\circ\text{C}$, (b) $T = 230\text{ }^\circ\text{C}$.

inspection of the $g(r)$ functions of figure 4 suggests that a simple expression will suffice, namely

$$f_1(Q) = 1 + A_1[\sin(Qr_1)/(Qr_1)] \exp(-Q^2u_1^2) + A_2[\sin(Qr_2)/(Qr_2)] \exp(-Q^2u_2^2) \quad (2)$$

which is the expression obtained by Fourier transforming two (slightly) broadened δ -functions in r -space. The areas of the δ -function peaks are A_1 and A_2 , their positions are r_1 and r_2 , while their widths are proportional to the parameters u_1 and u_2 . We expect this form for $f_1(Q)$ with any molecular model (ring or chain types) which has at least $1 + A_1 + A_2$ atoms per unit. The difference in the models lies in the values of A_1 and A_2 particularly, and hence absolute measurements of these quantities are the key data. Several fitting procedures were tried (in both Q -space and r -space), and it was found that the parameters A_1 , r_1 and u_1 could be determined reasonably well. However, because of coupling between parameters and because the second peak in $g(r)$ is not completely separated from the remainder, it is reasonable to quote a coupled set of parameters (with approximate errors) which will delete the second peak in $g(r)$ in a reasonable way. Effectively this means that it is not worthwhile extending the series (2) to higher terms. The parameters used in equation (2) are listed in table 1. Figure 5 shows the resulting data for $S_D(Q)$. Its Fourier transform $g_D(r)$ is shown in figures 6(a) and (b). It should be noted that over the range of r from 0 to 3.6 \AA , $g_D(r)$ is essentially zero so

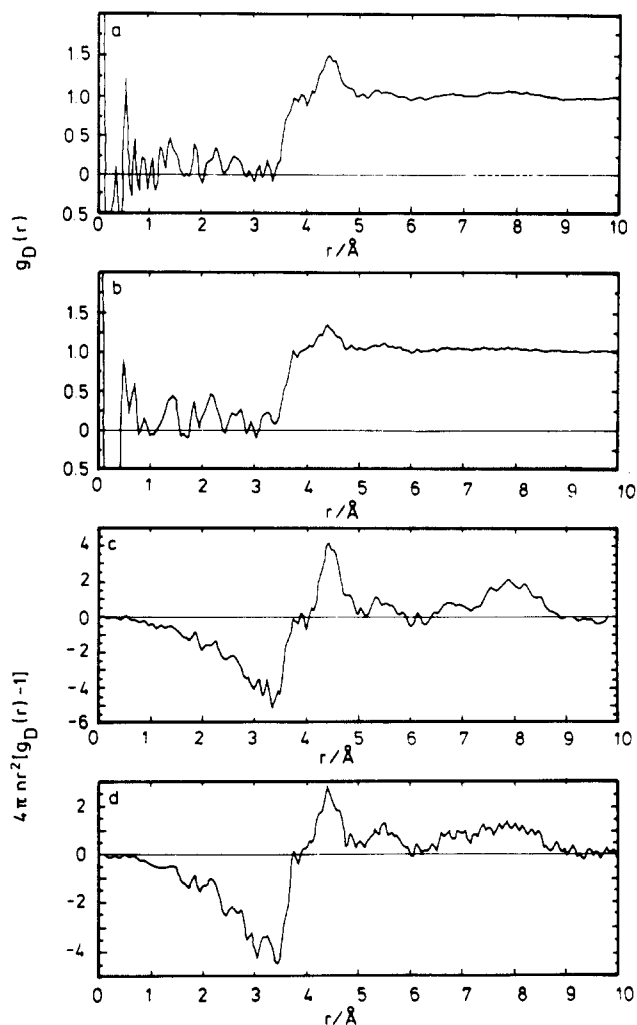


Figure 6. The pair correlation function $g_D(r)$ at (a) $T = 150$ °C and (b) $T = 230$ °C. These data are expressed in the form $4\pi r^2 n(g_D(r) - 1)$ described at equation (3), at (c) $T = 150$ °C and (d) $T = 230$ °C. Note different scales for (c) and (d). By comparing these data with those of figure 4 note how completely the first two sharp temperature independent peaks in $g(r)$ have been removed.

that the areas in table 1 include any intermolecular intensity in this r -range. However, as explained above this is not a large effect.

In order to bring out details at higher r -values, and to remove the number density n from the presentation we have plotted (in figure 6(c) and (d)):

$$4\pi r^2 n(g_D(r) - 1) = (2\pi/r) \int S_D(Q) Q \sin(Qr) dQ. \quad (3)$$

This function gives the fluctuation from the mean value of the number density.

From table 1 it is notable that slightly less than two atoms are found in the peak at 2.06 Å, which indicates that the local liquid structure is broken up compared to the

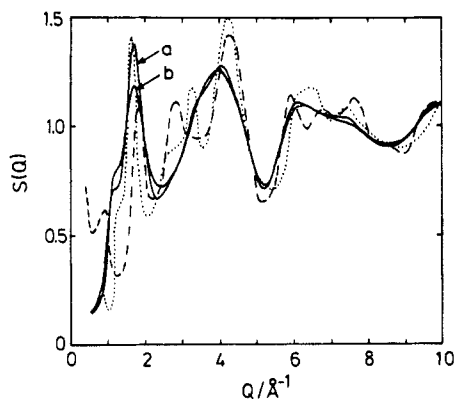


Figure 7. Comparison of the experimental structure factor of liquid sulphur at (a) $T = 150\text{ }^{\circ}\text{C}$, (b) $T = 230\text{ }^{\circ}\text{C}$ (full curves) with the packed ring model (dotted curve) and relaxed packed chain model (dashed curve) of Popescu [37].

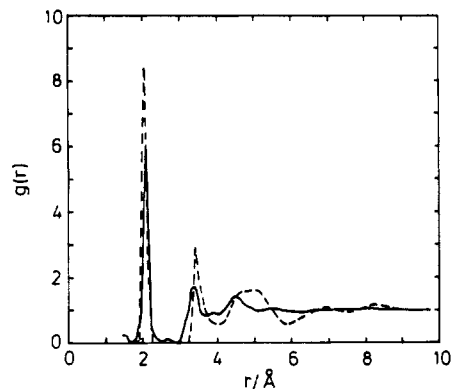


Figure 8. Comparison of the experimental pair distribution function $g(r)$ of liquid sulphur at $T = 150\text{ }^{\circ}\text{C}$ (full curve) with the S_8 -model of Stillinger *et al* [34] (dashed curve).

crystalline case. It is worth noting that (for example) a system of broken S_8 or S_{20} rings would yield an area of 1.75 or 1.90 at this distance respectively. The two peaks listed in table 1 are the only ones which are sharp and nearly temperature independent, and we note that they cover only about 6 atoms. Consequently this is approximately the number of atoms which may be thought of as pseudo-molecule. If the peak at 4.45 Å in figures 6(c) and (d) represents another part of this molecule (even though it is broader and is temperature dependent) then at 150 °C the molecule would contain about eight atoms and at 230 °C it would contain seven atoms, after subtracting a reasonable temperature dependent background in $g(r)$ on the basis of the solid state structure.

We have compared our data (particularly figures 3 and 4) with the S_8 model of Stillinger *et al* [34] and the models of Popescu [36] for packed polymer sulphur chains and rings in figure 7 and 8. It seems that none of the simple models like S_8 rings or freely rotating packed chains for liquid sulphur agree satisfactorily with the experimental shapes for both liquid temperatures.

In the absence of such a model we tried a (probably) oversimplified form of analysis, assuming again that a pseudo-molecular unit exists in the liquid and moreover that it is approximately spherical. Because in equation (2) we find that A_2 is greater than the values expected for rings or chains, we may expect the observed unit to be more spherical than for conventional models. In this case the structure factor may be approximated by a form often used for molecular systems [43, 44], and for which the spherical distribution of scattering power means that the form factor for a single molecule $f_1(Q)$ is the same function as the pair distribution form factor. Thus in this approximation:

$$S_m(Q) \approx f_1(Q)S_c(Q) \quad (4)$$

where $S_m(Q)$ is the structure factor for the molecular liquid, $f_1(Q)$ is given at equation (2) and $S_c(Q)$ is the structure factor for molecular centres. At figure 5 we have compared the structure factor $S_c(Q)$ to $S_D(Q)$ from equation (1). It can be seen that both functions are much closer to the structure factor for a simple atomic fluid (e.g. Ar) than is the function $S_m(Q)$. Also they are quite similar to one another for $Q > 2\text{ }\text{\AA}^{-1}$, and for

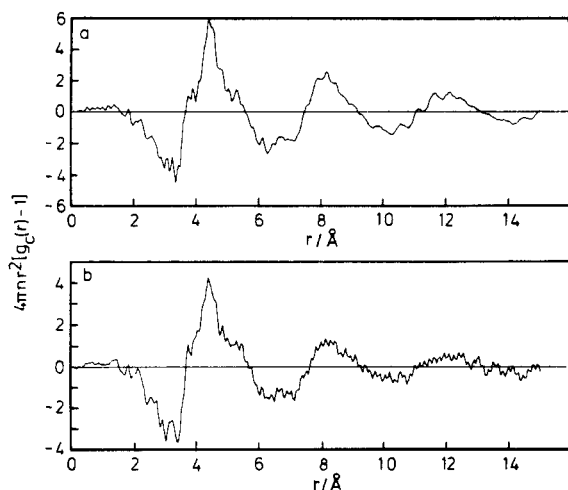


Figure 9. The pair correlation functions for the $S_c(Q)$ cases shown in figure 5 expressed as $4\pi n^2 n(g_c(r) - 1)$. (a) $T = 150^\circ\text{C}$, (b) $T = 230^\circ\text{C}$.

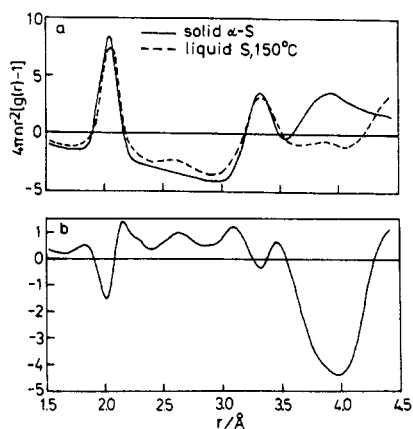


Figure 10. A comparison of $4\pi n^2(g(r) - 1)$ for the liquid at 150°C with the same function for the crystalline α -solid at room temperature (calculated). (a) $4\pi n^2(g(r) - 1)$ for the liquid (dashed line) and for the α -solid (full line); (b) difference (liquid minus solid) between the two curves shown in (a).

$Q < 2 \text{ \AA}^{-1}$ the function $S_c(Q)$ is closer to a physically realistic structure factor. Thus, qualitatively, $S_c(Q)$ exhibits the feature suggested by this model. In figure 9 we show the pair correlation functions for the $S_c(Q)$ data of figure 5. It is seen that they are oscillatory functions similar to those expected for a simple fluid; and the amplitudes of the oscillations decrease with increasing temperature.

It should be pointed out that the $Q \rightarrow 0$ limit of $S_c(Q)$ is readily calculated, and is related to the area of the functions plotted in figure 9. In order to obtain the correct value of $S_c(Q \rightarrow 0)$ (calculated by using the formula $S_m(Q) \rightarrow nk_B T \chi_T$ as $Q \rightarrow 0$, in equation (4)), the mean level of $g_c(r) - 1$ over the range 4 to 8 Å (for example) would need to be slightly negative. But it is difficult to check this feature with data (even) of the present high quality.

An insight into the liquid structure may be also gained by comparing the pair distribution functions for the liquid and the solid. The pair distribution function calculated from the published crystal structure of α -sulphur [45] is compared to the liquid data at 150°C in figure 10. At the nearest neighbour peak at 2.05 Å the data coincide apart from a small shift to higher r in the case of the liquid. Also the next peak at 3.3 Å is wider for the liquid than for the solid as expected, and the intensity for the liquid is greater than for the solid. The major difference between the solid and the liquid is the disappearance of the intensity at 3.8 Å and the appearance of extra intensity in the 3.3 Å peak and also at lower r . The extra intensity at distances between 2 and 3.5 Å suggests that S_8 molecules deform or break up, which in particular enhances the 3.3 Å distances in the molecules. The peaks at 3.8 Å, and a similar one at 5.5 Å, in the solid are due to correlations between an atom in one ring and other atoms in different rings. Both peaks broaden significantly and decrease in height on melting. This behaviour is consistent with both an increase in disorder and a possible opening of some rings. These comments

are consistent with a picture of the liquid at 150 °C in which small molecular units change shapes to fill the available volume (so causing the density to vary more slowly with temperature [4, 7] and the peak height of $S_m(Q)$ to fall (see figure 2). Thus the λ -transition might be associated with a percolation limit for the bonds/or the molecular units. However, this topic requires a more general investigation.

5. Conclusion

Accurate modern diffraction results measured with modern instruments allow good quality data on the pair correlation function for liquid sulphur to be obtained. These data permit molecular models to be tested and it has been shown that they are inconsistent with the existing conventional models for liquid sulphur.

Also, the observed structure factor of liquid sulphur may be directly analysed into molecular species more simply than trying to employ models of rings and chains. If simplicity in the shape of $S_c(Q)$ and $g_c(r)$ is an important requirement, it would appear that the liquid 'molecule' contains approximately six atoms. As the structural parameters of liquid sulphur below and above the λ -transition temperature differ only slightly, one might infer that the difference between these two regimes is only due to different sizes of these pseudo-molecular units, and perhaps changes in their thermal motion. Thus it is possible that the high viscosity at $T > 160$ °C, could be due to a percolation limit being reached for these pseudo-molecules. When the molecular units expand or change shape to fill the available free volume the percolation limit is reached and the viscosity rises. The internal dimensions found for the sulphur 'molecule' (i.e. 2.06 Å and 3.35 Å) are similar to those found in the solid state (2.05 Å and 3.33 Å [4]). If each 'molecule' consists of broken fragments, from parts of S_8 rings or polymeric chains, this would not be surprising. Also it would be expected that any sulphur atom would move from 'molecule' to 'molecule', which would tend to account for the values of the constants A_1 and A_2 in table 1. The broad liquid-like peaks in the radial distribution function left after removal of the molecular structure, represent the underlying liquid structure. Their spacing of about 4.3 Å is also consistent with this picture. The liquid structure is clearly temperature dependent, in contrast to the temperature independence of the molecular structure. Calculations of other properties (e.g. the specific heat) for this model are beyond the scope of this paper and require, for example, the definition of the vibrational properties in addition to the structure.

Thus we conclude that neutron diffraction experiments are a valuable tool for studying sulphur, especially because they observe the liquid itself and determine quantitatively the local environment around a central atom by direct observation. Consequently this method is in contrast to many conventional methods which attempt to obtain similar data by indirect analysis.

Acknowledgments

We are happy to acknowledge the help and support of the staff at the NRU reactor in Chalk River and at the ISIS pulsed neutron source of the Rutherford Appleton Laboratory. We would like to thank Dr C Wilson for assistance in calculating $g(r)$ for the α -solid.

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