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The structural properties of liquid, solid and amorphous sulphur

R Winter[†], P A Egelstaff[‡], W-C Pilgrim[†] and W S Howells[§]

[†] Institute of Physical Chemistry, University of Marburg, D-3550 Marburg, Federal Republic of Germany

[‡] Physics Department, University of Guelph, Guelph, Ontario N1G 2W1, Canada

[§] Rutherford Appleton Laboratory, Didcot, Oxon OX11 0QX, UK

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Abstract. A series of neutron diffraction experiments have been used to investigate the properties of liquid, solid and amorphous sulphur. The liquid was studied from 131 °C to 230 °C, i.e. at conditions around the λ -transition ($T_\lambda = 159$ °C). The amorphous sample was studied at -196 °C and the crystalline solid at room temperature. The data have been transformed to give an accurate pair correlation function $g(r)$ from which the absolute numbers of atoms in given molecular configurations may be determined for distances less than 8 Å. A comparison of the solid and liquid $g(r)$ data indicates which intermolecular bonds are broken on melting. The liquid data seem to be inconsistent with the picture of 'crown'-shaped S_8 molecules below T_λ , and with the proposed S_8 -to-polymer transition at T_λ . Also it has been found that the diffraction pattern may be analyzed 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 these units. The amorphous material was studied at the quenching temperature of -196 °C and its structure is intermediate between that of the parent liquid and the crystalline solid. It is concluded that a fundamental diffraction analysis of the states of sulphur has thrown new light on long standing problems.

1. Introduction

The investigation 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]. The stable crystalline modification at room temperature is orthorhombic sulphur (S_α), which consists of S_8 rings as structural units with an average bond length of 2.05 Å [1]. It melts at about 115 °C and it is believed that this liquid is made up mainly of S_8 ring molecules, too [2, 3]. At 159 °C a phase transition occurs in the melt, which is e.g. indicated by a drastic increase of the viscosity. This so-called λ -transition is thought to be due to the conversion of some S_8 rings to long polymer chains [1-3].

The structure of sulphur in its liquid and quenched states has attracted considerable experimental [1, 4-8] as well as theoretical [9-12] attention for many decades. However, still no model accounts satisfactorily for all its properties. To obtain a better understanding of this system we performed a variety of diffraction experiments. In this paper

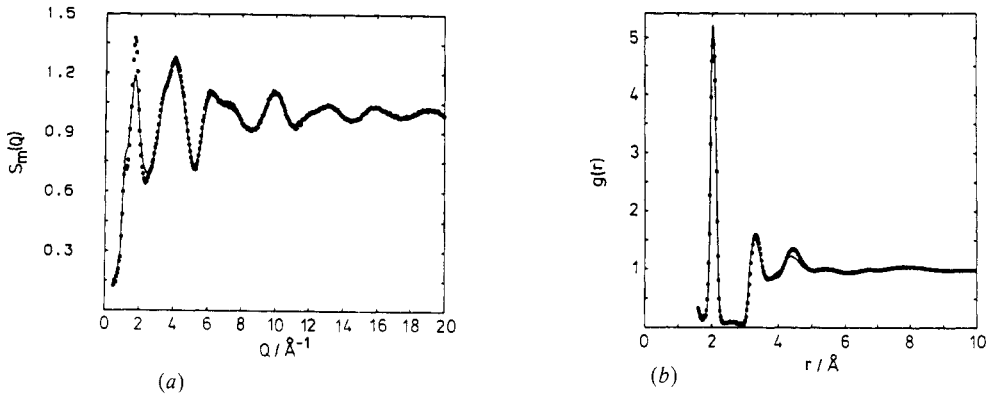


Figure 1. (a) The molecular structure factor $S_m(Q)$ of liquid sulphur at $T = 150\text{ °C}$ (dots) and 230 °C (full curve). (The measurements were performed at the LAD instrument at the ISIS accelerator at the Rutherford Appleton Laboratory up to 40 Å^{-1} .) (b) The pair correlation function $g(r)$ of liquid sulphur for 150 °C (dots) and 230 °C (full curve).

we describe the results on crystalline, amorphous and also on liquid sulphur in the temperature range of 131 °C – 230 °C , i.e. around the λ -transition.

2. Results and discussion

Figure 1 depicts the measured molecular structure factor $S_m(Q)$ and its Fourier transform $g(r)$ for liquid sulphur at, e.g., 150 °C and 230 °C , i.e. at a condition below and above the λ -transition. Altogether, a series of nine temperatures has been measured around T_λ [7]. From these diffraction experiments it is obvious that the structural changes accompanying this transition are relatively small. Each of the $g(r)$ curves shows about two nearest neighbours centred around 2.06 Å and a second concentration of roughly three atoms at a distance of about 3.35 Å . Whereas these peaks at the first two distances are almost independent of temperature, the third peak for the liquid around 4.45 Å is broad and decreases with increasing temperature.

There have been several attempts to model liquid sulphur [5, 11, 12]. 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. However, it seems that none of these models agrees satisfactorily with the experimental shapes for both liquid temperatures.

In the absence of such a model we tried a (probably) oversimplified form of analysis by using a molecular type of model. We assume that a pseudo-molecular unit exists in the liquid and moreover that it is approximately spherical, so that $S_m(Q) \approx f_1(Q)S_c(Q)$, where $f_1(Q)$ is the molecular form factor for the pseudo-molecular unit and $S_c(Q)$ is the ‘centres’ structure factor [13, 14]. Molecular units are expected to produce sharp peaks at low r in $g(r)$, which are fairly independent of temperature. The inspection of the $g(r)$ functions of figure 1(b) suggests that the first two peaks 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 a

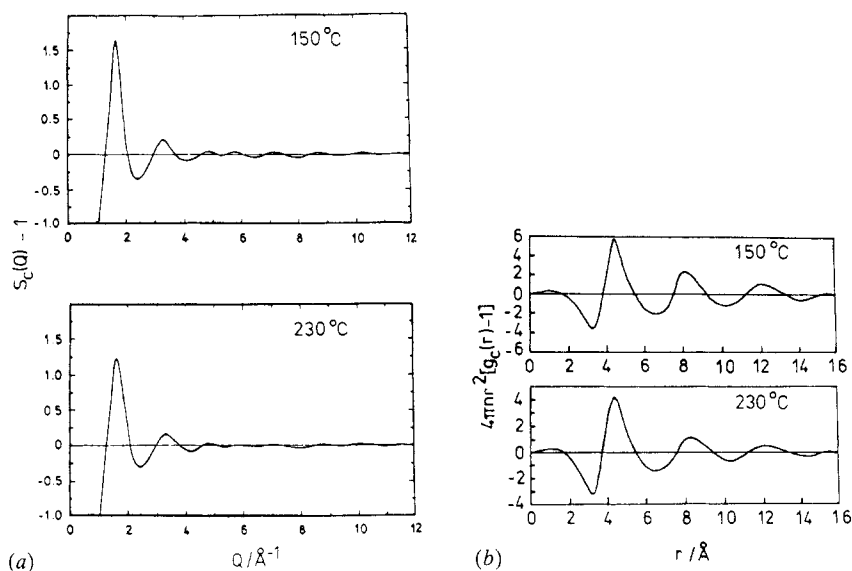


Figure 2. (a) The structure factor of molecular centres $S_c(Q)$ at $T = 150^\circ\text{C}$ and $T = 230^\circ\text{C}$. (b) The pair correlation functions for the $S_c(Q)$ cases, expressed as $4\pi r^2 n [g_c(r) - 1]$.

pseudo-molecule and thus contribute to $f_1(Q)$. At figure 2 we show the resulting structure factors $S_c(Q)$ and its pair correlation functions $g_c(r)$. It can be seen that both functions are close to those for a simple atomic fluid, like liquid argon. The broad liquid-like peaks in the radial distribution function left after removal of the molecular structure represent the underlying liquid structure and the amplitudes of the oscillations decrease with increasing temperature, as expected. Thus, qualitatively, $S_c(Q)$ and $g_c(r)$ exhibit the features suggested by this model and hence this simple model may be a plausible solution.

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 $T > 159^\circ\text{C}$, could be due to a percolation limit being reached for these pseudo-molecules. 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'. However, this topic requires a more general investigation as well as precise theoretical calculations.

Recently, we have also shown by neutron diffraction experiments, that a truly amorphous solid form of sulphur can be made by quenching liquid sulphur into liquid nitrogen [15]. Its structure factor is similar to that for the parent liquid. The only difference is that the small shoulder on the liquid curve at 1.2\AA^{-1} is hardly seen in the amorphous case, and the peak at about 6.5\AA^{-1} has developed into a doublet in the amorphous curve. The corresponding pair correlation function $g(r)$ is shown in figure 3. The interesting feature is the growth of peaks at 3.9\AA and 5.4\AA in comparison to the liquid $g(r)$ (see figure 1(b)). At a temperature above about -20°C , however, the amorphous sulphur structure changes again, plastic sulphur is formed, which slowly converts to a mixture of crystalline polymeric and S_a -sulphur [1, 7, 15].

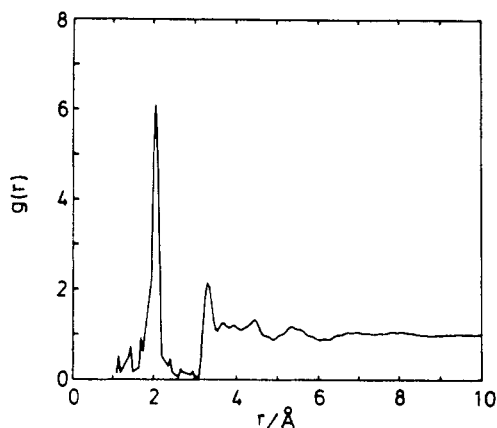


Figure 3. The pair correlation function $g(r)$ for the amorphous sulphur experimental data [15]. (These measurements were performed at the D4B instrument of the Institut Laue–Langevin, Grenoble.)

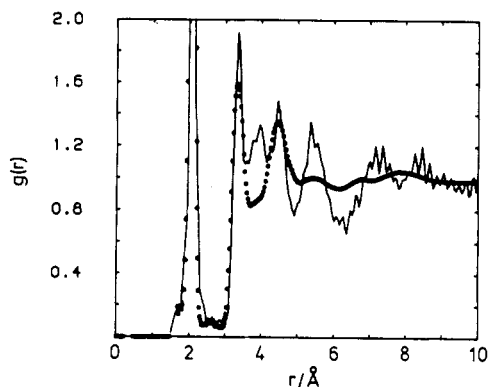


Figure 4. A comparison of $g(r)$ for the liquid at 150 °C (dots) with the same function for the crystalline S_{α} solid (full curve). (The data for the crystalline solid were obtained on the LAD instrument at ISIS, Rutherford Appleton Laboratory.)

A further insight into the difference of the amorphous to the liquid structure may be gained by comparing their $g(r)$ s also with that of crystalline S_{α} . As can be seen from figure 4, at the nearest neighbour peak at 2.05 Å and at 3.3 Å, the data of the liquid and S_{α} coincide. The major difference between the solid and the liquid is the disappearance of the intensity at 3.9 Å and 5.4 Å in the liquid. This indicates that the intermolecular bonds at 3.9 Å and 5.4 Å are broken on melting, only, and by comparing figure 4 with figure 3 it can be seen that the amorphous sulphur state is intermediate between that of the parent liquid and the crystalline solid.

References

- [1] Meyer B 1965 *Elemental Sulfur* (New York: Interscience)
- [2] Ward A T 1968 *J. Phys. Chem.* **72** 4133
- [3] Steudel R and Mäusle H-J 1981 *Z. Anorg. Allg. Chem.* **478** 139
- [4] Thompson C W and Gingrich N S 1959 *J. Chem. Phys.* **31** 1598
- [5] Poltavtsev Yu G and Titenko Yu V 1975 *Russ. J. Phys. Chem.* **49** 178
- [6] Vahvaselkä K S and Mangs J M 1988 *Phys. Scr.* **38** 737
- [7] Winter R, Bodensteiner T, Szornel C and Egelstaff P A 1988 *J. Non-Cryst. Solids* **106** 100
- [8] Bellisent R, Descotes L, Boue F and Pfeuty P 1990 *Phys. Rev. B* **41** 2135
- [9] Petschek R G, Pfeuty P and Wheeler J C 1986 *Phys. Rev. A* **34** 2391
- [10] Stillinger F H, Weber T A and La Violette R A 1986 *J. Chem. Phys.* **85** 6460
- [11] Malaurent J C and Dixmier J 1977 *Phys. Status Solidi a* **43** K61
- [12] Popescu M 1987 *J. Non-Cryst. Solids* **97 + 98** 187
- [13] Egelstaff P A 1967 *An Introduction to the Liquid State* (New York: Academic) ch 6
- [14] Powles J G 1973 *Adv. Phys.* **22** 1
- [15] Winter R, Pilgrim W-C, Egelstaff P A, Chieux P, Anlauf S and Hensel F 1990 *Europhys. Lett.* **11** 225