

# The Structure of Glassy and Liquid Sulfur Revisited

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**Abstract.** High energy x-ray experiments have been performed on liquid and glassy sulfur over a wide temperature range. Heating the elastic quenched glass above -9 °C and super-cooling liquid sulfur below 51 °C both resulted in crystallization to monoclinic sulfur. The average coordination number of the first shell in glassy sulfur determined from the pair distribution function is found to be  $1.90 \pm 0.05$ . This result is in good agreement with previous neutron and x-ray pair distribution function studies, and lends support to the recent proposal that there are a significant number of short chains in the low temperature liquid upon melting. Also, a non-negligible coordination number of  $0.20 \pm 0.04$  is found in the interstitial region between the first and second shells in glassy sulfur, similar to that found in the liquid. An increase in the third peak in the glassy pair distribution function at 4.47 Å associated with S<sub>8</sub>-rings indicates the percentage is higher in the quenched glass compared to the stable liquid. This casts doubt on previous estimations of the percentage of S<sub>8</sub>-rings present upon melting.

**Keywords:** Sulfur, X-Ray Diffraction, Pair Distribution Function, Lambda Transition, Glass Structure

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## 1. Introduction

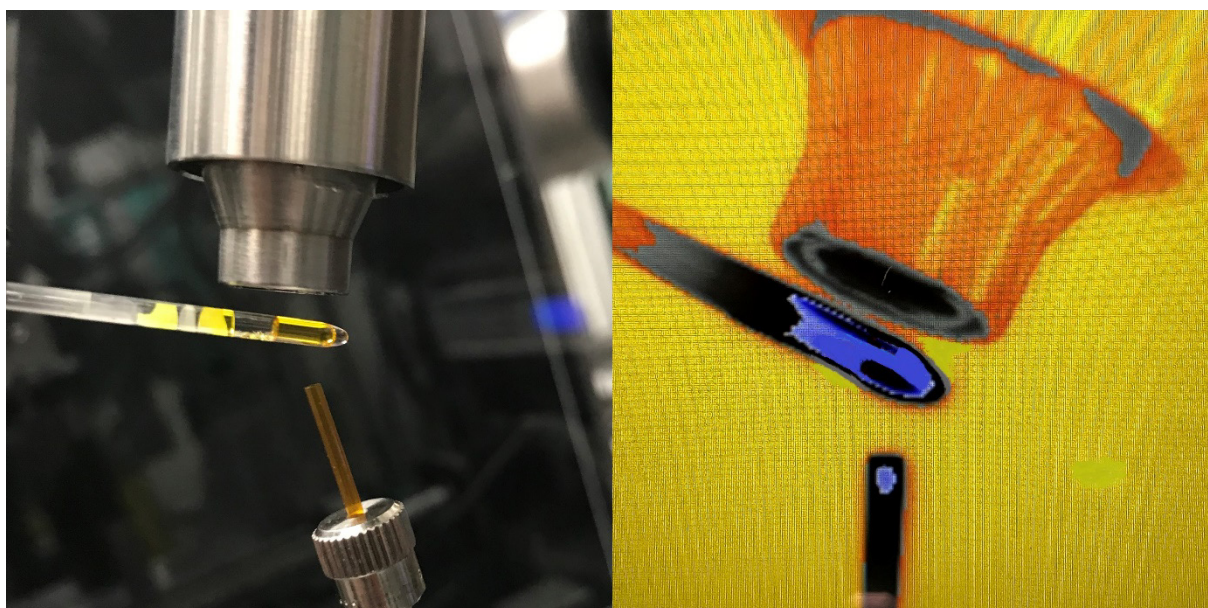
At room temperature the stable crystalline form of sulfur is orthorhombic ( $\alpha$ -S) which comprises solely of S<sub>8</sub> rings [1]. Just before melting monoclinic sulfur ( $\beta$ -S) is formed which also consists of only S<sub>8</sub> rings but in a different packing arrangement [2], [3]. Upon melting at 119 °C high performance liquid chromatography (HPLC), infra-red and Raman experiments have all suggested that the liquid is made up of mainly S<sub>8</sub> rings [4], [5], [6]. At the temperature  $T_\lambda = 159$  °C there is a dramatic increase in viscosity associated with a  $\lambda$ -transition as S<sub>8</sub> rings convert to long polymeric chains [7], [8], [9]. This is reflected in a change in many properties including the density, refractive index, thermal expansion and specific heat [6], [10], [11]. Rapidly quenching liquid sulfur from temperatures >159 °C results in a translucent glassy form known as “elastic sulfur” and is believed to comprise of a mixture of S<sub>8</sub> rings and polymeric chains [12], [13]. This glassy form of sulfur generally crystallizes into orthorhombic or monoclinic sulfur upon heating. In this study we have performed high energy x-ray experiments on both liquid and glassy sulfur over a wide temperature range. This work follows our recent findings that the coordination number of the first shell (at a bond distance of 2.06 Å) in liquid sulfur around the  $\lambda$ -transition is  $1.86 \pm 0.04$ , and not precisely 2.0 as widely accepted [4], [6], [13], [14], [15]. Our data agree

with a long list of x-ray and neutron pair distribution function (PDF) studies that consistently point towards the presence of a substantial number of under-coordinated sulfur atoms in the liquid state [16], [17], [18], [19], [20].

While it is generally accepted that the drastic increase in viscosity above  $T_\lambda$  arises from the breakup of  $S_8$  rings resulting in polymeric chain entanglement, experimental evidence for the mechanism by which this occurs has only recently been found [20]. Classical molecular dynamics simulations on liquid sulfur just above the melting point, show no intermolecular pairs in the “interstitial region” (2.32-2.9 Å) between the first and second shells [21]. This region was previously referred to as the forbidden zone because in monoclinic and orthorhombic sulfur the shortest distance between two  $S_8$  rings is just beyond the second shell distance at 3.35 Å. Nevertheless, both neutron and x-ray PDF studies have consistently found a small, but non-negligible intensity in the interstitial region, and this has been attributed to the existence of a significant number of short chains present in the liquid state upon melting. It has recently been proposed that the existence of terminal radicals associated with short chains are needed to initiate the bond exchange mechanism that breaks up  $S_8$  rings and results in the polymerization of chains in liquid sulfur above  $T_\lambda$  [22]. The main goals of this study are to ascertain if an undercoordinated first shell and interstitial atoms persist in glassy (elastic) sulfur.

## 2. Methods

Two separate high energy x-ray experiments were performed on glassy and liquid sulfur samples at cryogenic and hot temperatures using beamline 6-ID-D at the Advanced Photon Source, Chicago, USA. Both sets of measurements were performed on high purity sulfur samples (Alfa Aesar, 99.9995%) that were vacuum sealed in 2.0 mm inner diameter, and 2.4 mm outer diameter, quartz capillaries. The cryogenic experiments on supercooled sulfur were carried out cooling from 126 °C to 51 °C, and heating a glassy sulfur sample (quenched in liquid nitrogen from a temperature of 220 °C) from -55 °C to -9 °C in approximately 5 °C steps using a heater/nitrogen gas jet from an Oxford Cryostream 800, see Figure 1. All x-ray measurements had an equilibration time of 5 minutes at each temperature, followed by 5 minutes of data acquisition time. The surface temperature of the sample measured using a FLIR A325sc thermal infrared camera and the diffraction experiments used an incident x-ray energy of 86.89 keV (0.1427 Å). The high temperature experiments on molten sulfur were performed using a custom furnace, heating from 120 °C to 330 °C in 10 °C steps using an incident x-ray energy of 99.96 keV (0.1240 Å).

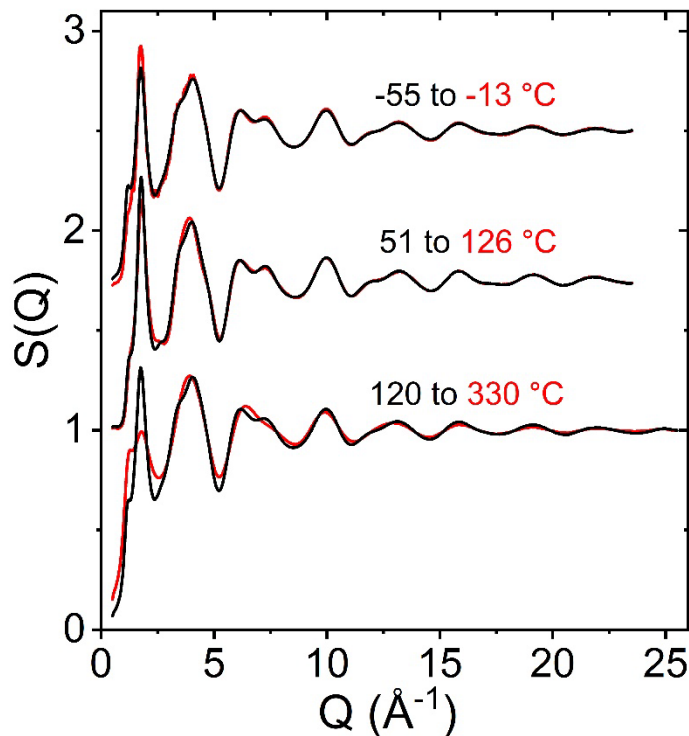


**Figure 1.** The cryostream diffraction set up with area detector in the background, and an image from the thermal imaging camera.

The scattered beam was recorded using a Varex (CT4343) area detector calibrated using a NIST standard  $\text{CeO}_2$  powder. The diffraction data were reduced using *Fit2D* [23] and *PDFgetX2* [24] software packages as described in [25], [26] and example structure factors,  $S(Q)$ , are shown in Figure 2. The densities for the liquid were taken from [27], [28], [29] and extrapolated to the glassy region.

### 3. Results

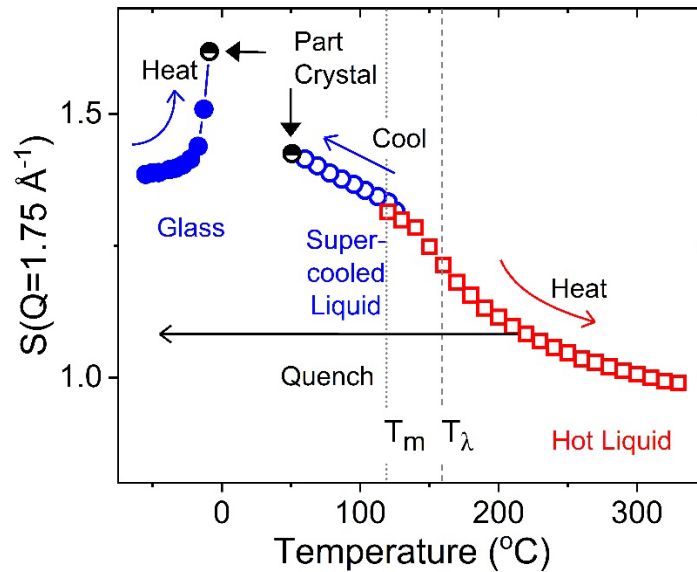
Glassy sulfur was obtained by quenching the liquid from 220 °C and was measured upon heating from the lowest temperature of -55 °C. The sample eventually partially crystallized at -9 °C into monoclinic sulfur. Quenching the liquid from 140 °C resulted in partial crystallization. Similarly, the supercooled liquid started to crystallize upon cooling at 51 °C into primarily monoclinic sulfur together with a minority orthorhombic phase. The glass transition temperature  $T_g$  of pure polymeric sulfur is 75 °C, while fast-quenched (elastic) sulfur which comprises of both polymeric chains and  $\text{S}_8$  rings is known to be -30 °C [13], [17]. The temperature dependence of liquid and glassy sulfur is most clearly identified by the height of the principal peak in  $S(Q)$  at  $Q=1.75 \text{ \AA}^{-1}$  [15] as shown in Figure 3. Only very subtle changes occur at high  $Q$ -values, confirming the local coordination is invariant. Notably, the x-ray structure factors of glassy sulfur at -55 °C is found to be most similar to supercooled liquid sulfur at 69 °C (not shown).



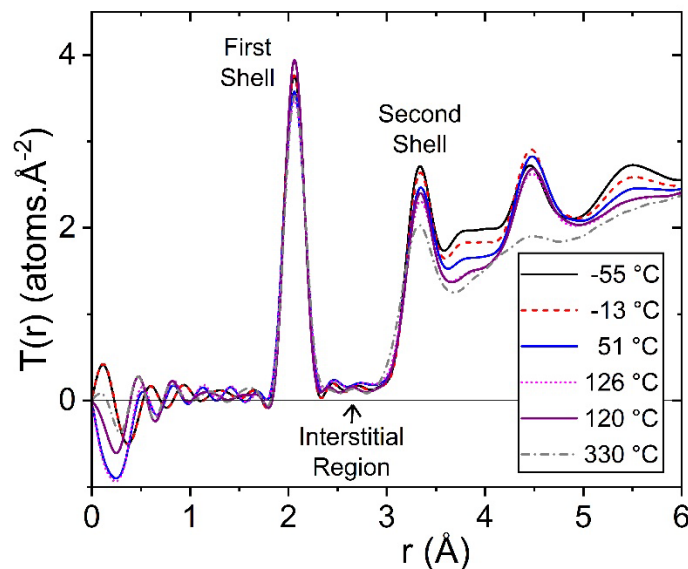
**Figure 2.** Selected x-ray structure factors covering three different measurement regions. The top two sets represent glassy and supercooled and stable liquid sulfur from -55 to -13 °C and +51 to +126 °C respectively, measured using the cryostream. The bottom set corresponds to liquid sulfur heated through the  $\lambda$ -transition to high temperatures, +120 to +330 °C. The hotter temperatures in each region are shown as red lines.

The total x-ray pair distribution functions, defined as  $T(r) = 4\pi\rho rG(r)$  [30], show the first peak in glassy sulfur to be at 2.06 Å and the second at 3.33 Å, see Figure 4. The third peak at

4.47 Å corresponds to the three furthest atom-atom distances within an S<sub>8</sub> crown shaped ring [1]. The intensities between the 2<sup>nd</sup> and 3<sup>rd</sup> peaks (at 4 Å) and beyond the third peak (at ~5.5 Å) increase with increasing density at lower temperatures. These distances correspond to inter-molecular distances between S<sub>8</sub> rings in orthorhombic and monoclinic sulfur. Previous Reverse Monte Carlo (RMC) and Empirical Potential Structure Refinement (EPSR) models of sulfur PDF data have been unable to unambiguously determine the structure of liquid [17], [31]. The inability to fit the interstitial region using RMC has led to the conclusion that low temperature liquid sulfur (i.e. <159 °C) is not consistent with a model entirely made up of S<sub>8</sub> rings [20].



**Figure 3.** The principal peak height in the x-ray structure factor corresponding to  $Q=1.75 \text{ \AA}^{-1}$  as a function of temperature. Glass quenched from 220 °C (solid blue circles), supercooled and stable liquid (open blue circles) and hot liquid (open red squares), see text. Partially crystallized  $S(Q)$ 's are shown as black and white circles. The melting temperature  $T_m$  is represented by the dotted line and the lambda transition  $T_\lambda$  by the dashed line.



**Figure 4.** The total x-ray pair distribution function at selected temperatures that span the three different temperature ranges measured.



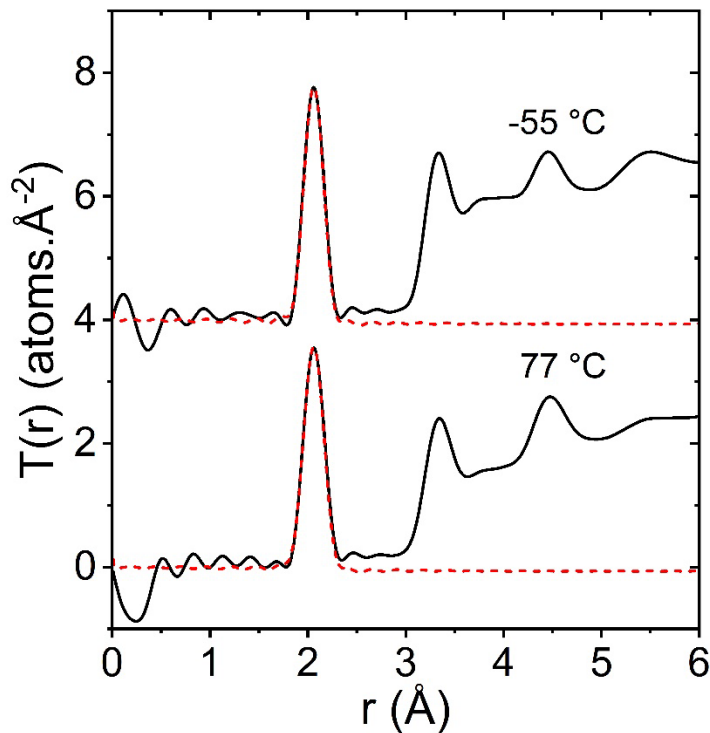
In our previous paper we have discussed in detail a number of possible sources of error that could affect the coordination number extracted from  $T(r)$  [20]. These include normalization issues, the shape of the electron cloud, and the instrumental resolution function. In this study the maximum uncertainty in the temperature measurements in the furnace and cryostream was  $\pm 2$  °C, corresponding to a density variation of  $\sim 0.2\%$ . A typical consistency check, used to verify that pair distribution function data is properly normalized, is to assess the level of the unphysical oscillations in the low  $r$ -region (below the first true peak,  $r_1$ ). These oscillations arise from Fourier transform artefacts associated with the finite  $Q$ -range, and any systematic errors in the experiment. For correctly normalized data these oscillations will vary around the bulk density, otherwise known as the Krogh-Moe-Norman normalization method [32], [33]. In the case of liquid sulfur, we find that the relatively flat level of intensity in the interstitial region (between 2.3-2.8 Å) is significantly higher than that the level observed in the unphysical region  $< 1.8$  Å (see Figure 5).

Here, the coordination number of the first peak in the pair distribution function was obtained by two methods (i) integrating between the minima either side of the peak with  $r_{\min}=1.80$  and  $r_{\max}=2.32$  Å and (ii) representing the peak by a Gaussian in  $Q$ -space and Sine Fourier transforming at the same  $Q_{\max}$  as the experimental data as shown in Figure 5. For a monatomic glass, the first shell between pairs of atoms in real space can be written in  $Q$ -space as,

$$P_1(Q) = N_1 \frac{\sin(Qr_1)}{Qr_1} \exp\left(\frac{-Q^2\sigma_1^2}{2}\right) \quad (1)$$

Where  $N_1$  is the coordination number of the first shell,  $r_1$  is the atomic separation and  $\sigma$  is the disorder parameter. Both methods gave the same results for the coordination number.

In this study we find that fast-quenched glassy sulfur at  $-55$  °C has a first shell coordination number of  $1.90 \pm 0.05$  compared to  $1.88 \pm 0.05$  for liquid sulfur at  $150$  °C. These results are in good agreement with previous studies. A comparison of the first shell coordination numbers for low temperature liquid and glassy sulfur measured by various authors using both neutrons and x-rays is given in Table 1.



**Figure 5.** Examples of Gaussian fits to the first shell constructed in  $Q$ -space and Sine Fourier transformed at the same  $Q_{max}$  (dashed red lines, see text) as the x-ray data (solid black lines) for glassy and supercooled liquid sulfur.

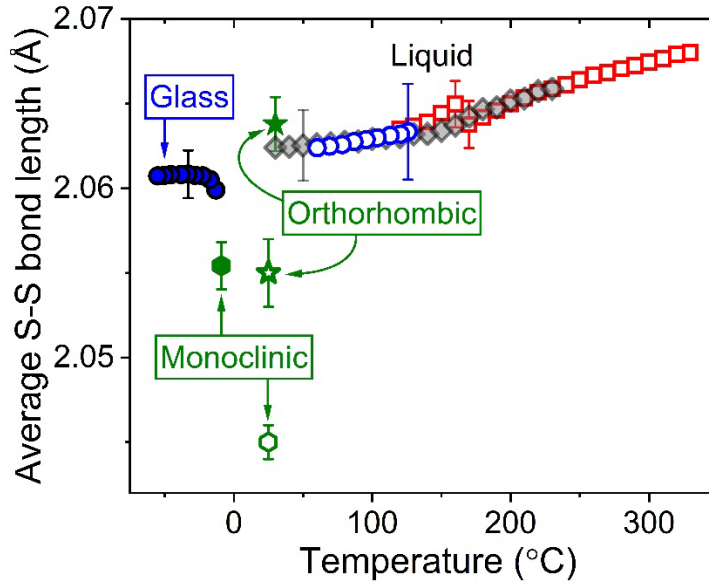
**Table 1.** Summary of the first shell coordination numbers in liquid and glassy sulfur obtained from x-ray and neutron diffraction studies. \* denotes coordination number determination by both integration in  $r$ -space and Gaussian fitting in  $Q$ -space which gave identical results.

Form	Temp (°C)	$N_1$	Technique	Reference
Liquid	150	1.88*±0.05	X-ray	This Study
Liquid	150	1.86±0.04	X-ray	Benmore <i>et al.</i> [20]
Liquid	150	1.85	X-ray	Zhang <i>et al.</i> [19]
Liquid	150	1.85	X-ray	Bellissent <i>et al.</i> [16]
Liquid	150	1.80±0.1	Neutron	Winter <i>et al.</i> [18]
Liquid	140	1.86±0.1	Neutron	Stoltz <i>et al.</i> [17]
Glass	-51	1.90*±0.05	X-ray	This Study
Amorphous	29	1.91	X-ray	Zhang <i>et al.</i> [19]

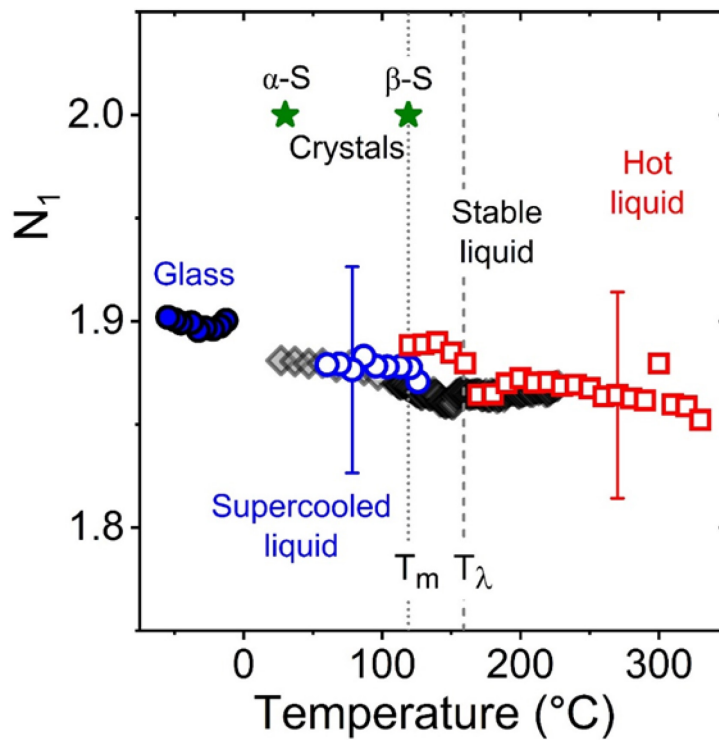
## 4. Discussion

Orthorhombic  $\alpha$ -S is the most stable crystalline form of sulfur and comprises of sixteen  $S_8$  crown shaped rings in the unit cell. The mean S–S bond length is 2.055 Å and mean S-S-S angle is 108.2° [1]. The monoclinic ( $\beta$ -S) phase forms above 95.4°C and contains six crown  $S_8$  rings in the unit cell, of which two are in disordered positions [2], [3]. The bond lengths here are almost equal at 2.045 Å, although the bond angles range from 106.5° to 109.3°. Both  $\alpha$ -S and  $\beta$ -S have minimum intermolecular  $S_8$ - $S_8$  contacts of 3.38 Å. Like selenium, viscous polymeric sulfur quenched from 250 °C forms a glass (sometimes known as plastic sulfur [12]) which has rubbery properties attributed to the presence of long helices [11]. The structure of quenched glassy sulfur has been studied by high resolution neutron diffraction and revealed an increase in intensity in the interstitial region between the first and second shells compared to the liquid state [17], although absolute coordination numbers were not determined. The additional interstitial intensity was attributed to ‘more broken bonds’ [17].

S-S bonds are extremely flexible, and their bond lengths can vary immensely, between distances of 1.8 to 3.0 Å [34]. Density function theory calculations predict that S-S bonds can range from 1.925 to 2.331 Å within different types of  $S_8$  molecules alone [6]. In the liquid state, the modeling of high-resolution neutron diffraction data has revealed that  $S_8$  rings are heavily distorted from the crown shape found in the crystalline form [17]. So, while terminal S-S bonds in polymer chains do have shorter bonds than those in the middle of the chain [6], they still lie within the range of S-S bond distances within a dynamically distorted  $S_8$  molecule. The variation in S-S bond length is demonstrated in the difference observed in the average orthorhombic and monoclinic forms shown in Figure 6. We note here that the average S-S distances obtained using PDF are longer than those obtained from crystallographic refinements. This reflects the difference associated with a crystal structure that is dynamically disordered, such that the time-averaged periodic structure (from Rietveld refinement) and instantaneous local structures (from the PDF) can be significantly different. [35]. A slight discontinuity in the S-S bond length at  $T_\lambda$  in the furnace measurements of this study was not observed in our previous measurements [20], although the variation is within the size of the error-bars. The corresponding average first shell coordination number obtained through integration is shown in Figure 7.

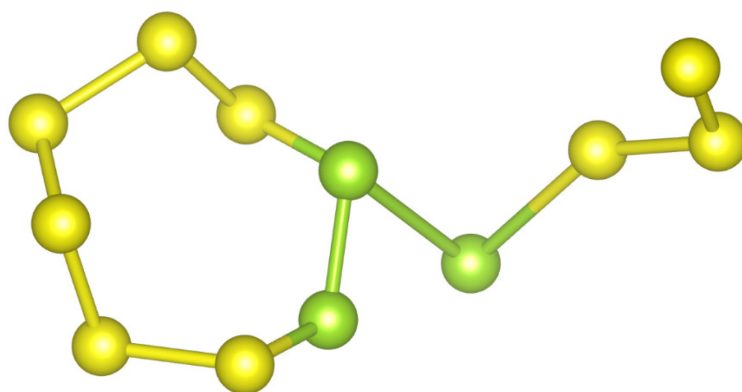


**Figure 6.** The average S-S bond length as a function of temperature. Glass and deeply supercooled liquid (filled blue circles), supercooled and low temperature liquid sulfur (open blue circles) and hot liquid sulfur above the  $\lambda$ -transition (open red squares). The data from Benmore et al. [20] are shown as grey diamonds, renormalized by a factor of 1.0022. Monoclinic sulfur (green hexagons) and Orthorhombic sulfur (green stars) obtained from PDF (filled symbols) and crystallography (open symbols), see text.



**Figure 7.** The first shell coordination number for glassy sulfur (filled blue circles, this study), supercooled and low temperature liquid sulfur (open blue circles, this study) and hot liquid sulfur above the  $\lambda$ -transition (open red squares, this study).  $N_1$  was obtained by integrating between 1.80 and 2.32 Å. The data from Benmore et al. [20] are shown as grey diamonds obtained using the same criteria. Monoclinic sulfur and Orthorhombic sulfur are shown as green stars. The melting temperature  $T_m$  is represented by the dotted line and the lambda transition  $T_\lambda$  by the dashed line.

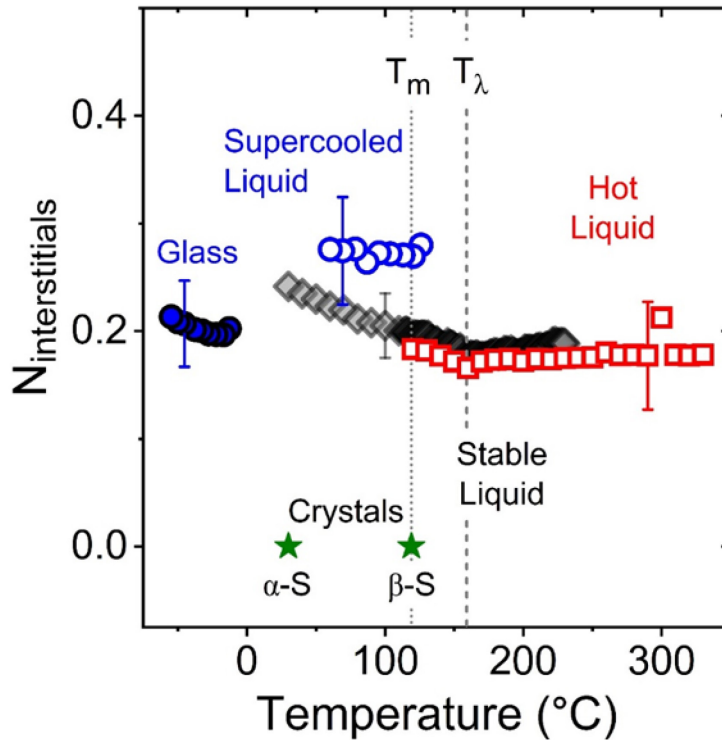
A multitude of infra-red, Raman and sound velocity measurements have demonstrated that the  $\lambda$ -transition can be characterized as a breakup of  $S_8$  rings and their subsequent polymerization [5], [10], [14], [36], [37]. Stillinger *et al.* first proposed an intermediate tadpole mechanism to explain the conversion from  $S_8$  rings to polymeric chains, see Figure 8 [21]. The tadpole represents a metastable reaction, whereby a terminal S atom on the end of a chain cleaves an  $S_8$  ring. This bond switching mechanism has been supported by Monte Carlo studies [38]. The existence of a metastable 3-coordinate sulfur atom is energetically unfavourable, however recent machine learning molecular dynamics indicate that the transformation between  $S_8$  rings to chains occurs very quickly, over nanosecond timescales [22]. A critical aspect of the thermally activated  $\lambda$ -transition depends on the existence of short sulfur chains in the liquid, whereby under-coordinated terminal atoms hold a concentration of negative charge capable of opening an  $S_8$  ring.



**Figure 8.** The proposed tadpole mechanism between short chains and  $S_8$  rings. The green atoms indicate those involved in the bonding change.

The coordination number associated with the interstitial region in glassy sulfur,  $N_{\text{interstitials}}$ , is found to be  $\sim 74\%$  of the intensity present in the supercooled liquid (when measured under the same experimental conditions), indicating a lower percentage of short chains and/or broken bonds in the glass compared to the liquid. This is despite the fact the absolute numbers obtained in our supercooled liquid measurements (open blue circles in Figure 9) show a significant systematic error compared to our previous work, albeit within the overall absolute error-bar. This is undoubtedly associated with the difficulty in extracting the small intensity in the interstitial region that is convoluted with Fourier transform oscillations. The random errors between adjacent scans during the same experiment are however substantially smaller, as demonstrated by the reproduction of the shallow minimum in  $N_{\text{interstitials}}$  at  $T_\lambda$  compared to our earlier study [20].



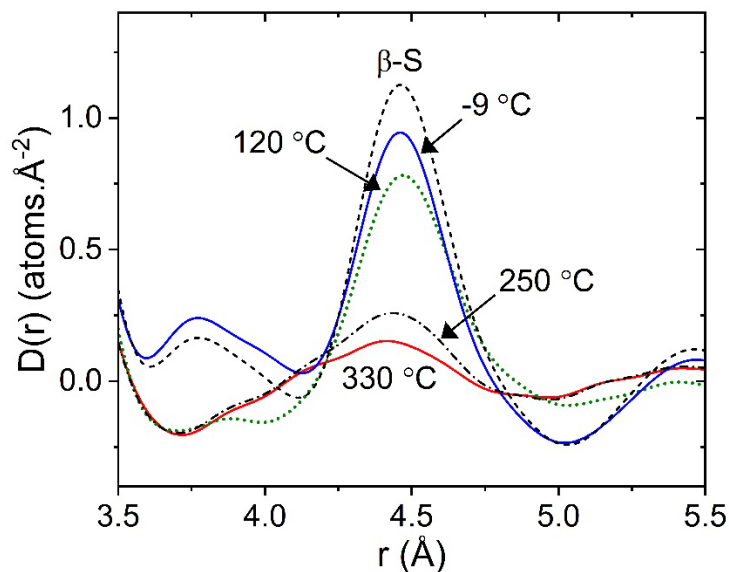


**Figure 9.** The interstitial coordination number corresponding to the intensity between the first and second shell for glassy sulfur (filled blue circles, this study), supercooled and low temperature liquid sulfur (open blue circles, this study) and hot liquid sulfur above the  $\lambda$ -transition (open red squares, this study).  $N_{\text{interstitials}}$  was obtained by integrating between 2.32 and 2.90 Å. The data from Benmore et al. [20] are shown as grey diamonds obtained using the same criteria. The melting temperature  $T_m$  is represented by the dotted line and the lambda transition  $T_{\lambda}$  by the dashed line.

It has been suggested that the presence of polymeric sulfur ( $S_{\mu}$ ) is a key factor to glass formation [4], and that only liquids quenched from temperatures  $>T_{\lambda}$  can readily form glasses. In this framework  $S_{\mu}$  represents long chains. This assertion is consistent with the measurements performed in this study, and is also supported by previous neutron diffraction experiments on nitrogen quenched liquid samples above and below  $T_{\lambda}$  [17]. The ratio of  $\phi(T) = S_{\mu}/(S_{\mu} + S_8)$  has been measured using Raman spectroscopy [4], [5], [7] and by HPLC chemical analyses of the insoluble content determined by dissolving quenched glassy sulfur in carbon disulfide [37]. Steudel [6] also used HPLC to determine the majority content of  $S_8$  rings (94%),  $S_7$  rings (3%) and other ring sizes ( $<<1\%$ ) in quenched sulfur. Recent density functional theory based molecular dynamics simulations with  $>96\%$  twofold sulfur predicts a nearly constant number of  $S_8$ -rings ( $\sim 53\%$ ) at  $T > T_{\lambda}$ , and accurately reproduces the temperature dependent fraction of  $S_{\mu}$  compared to these previously experimental works [15].

However, more recent x-ray diffraction experiments indicate a significant number of short chains ( $S_n$ ) are also present in the liquid, due to the degree of under-coordination found in the first peak i.e. 93% twofold [20]. Therefore, we have previously argued that the chain content (both  $S_{\mu} + S_n$ ) is substantially higher in liquid sulfur at  $T_{\lambda}$ . This is supported by the results from this work, since the first shell coordination number is found to be  $1.90 \pm 0.05$  in glassy sulfur, significantly lower than the value of 2.0 found in orthorhombic and monoclinic sulfur, see Figure 7. Notably, the 4.47 Å peak in the x-ray pair distribution function has been associated with the furthest atom-atom interactions across a crown shaped  $S_8$  ring i.e., including the 3<sup>rd</sup> nearest neighbors (two atoms at  $\sim 4.43$  Å) and 4<sup>th</sup> neighbor (one atom at  $\sim 4.65$  Å). In Figure 10 we observe an increase in intensity of the third peak at 4.47 Å upon quenching the liquid from 220  $^{\circ}\text{C}$  to the glassy state ( $< -30$   $^{\circ}\text{C}$ ), which indicates that the  $S_8$ -ring contents in the glassy state are significantly higher than those found in the stable liquid [16]. This finding has implications

for several existing models of based on the assumption that  $\phi(T_m) < 5\%$  in liquid sulfur upon melting [39] and will be discussed in detail in a future paper.



**Figure 10.** The differential x-ray pair distribution function for selected temperatures showing the temperature dependence of the 4.47 Å peak associated with the relative number of  $S_8$ -rings in the liquid, glass and monoclinic crystal.

## 5. Conclusions

High energy x-ray diffraction measurements have been conducted on glassy sulfur between  $-55$  and  $-13$  °C, and on liquid sulfur over a wide temperature range from  $330$  °C down to  $51$  °C into the supercooled regime. The average coordination number of the first shell in glassy sulfur is found to be  $1.90 \pm 0.05$  in good agreement with previous neutron and x-ray pair distribution function studies on both the liquid and glassy states. The number of interstitial atoms between the first and second shells in glassy sulfur is found to decrease slightly compared to the supercooled liquid, consistent with a higher  $S_8$  ring content compared to the stable liquid. The increase in intensity of the third peak in the glassy pair distribution function at  $4.47$  Å, which are associated with atom-atom distances across the crown shaped  $S_8$  ring, also suggest the number of  $S_8$  rings in the quenched glass is higher than that in the liquid at temperatures  $> T_m$ . This casts doubt on the previous determination of  $S_8$  ring contents in liquid sulfur from HPLC measurements on quenched samples. In addition, our results are consistent with a number of short chains alongside a majority of  $S_8$  rings in the glassy state. However, questions still remain. Is it possible to make a glass of pure sulfur that comprises purely of  $S_8$  rings? If not, what is the critical polymeric content  $\phi(T)$  necessary for glass formation? Finally, recent machine learning driven molecular dynamics simulations have successfully demonstrated the polymerization process from chains to polymeric chains on nanosecond timescales [22]. Nonetheless, a comprehensive structural model of low temperature liquid sulfur that agrees with all the available experimental data is still missing. The relatively subtle differences in first shell and interstitial coordination number in the liquid compared to the crystalline forms represent crucial constraints that need to be incorporated into any realistic model.

## Data availability statement

Data will be made available on request.

## Author contributions

Chris J. Benmore; Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Validation, Visualization, Writing – original draft, Writing – review & editing.

## Competing interests

The authors declare that they have no competing interests.

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