

Liquid sulfur: Local-order evidence of a polymerization transition

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The polymerization transition of liquid sulfur has been observed at the microscopic level, through a change in the local order as a function of the temperature. A diffraction measurement using hot source neutrons ($\lambda = 0.709 \text{ \AA}$) has been performed to determine the pair correlation function. The third peak of this pair correlation function exhibits a drastic drop with increasing temperature that reflects directly the decrease of the concentration of the sulfur atoms in the S_8 rings when the rings are progressively breaking into long chains.

Around a temperature $T_p = 160^\circ\text{C}$ liquid sulfur shows a sudden change which is associated with the equilibrium polymerization of very long chains out of the S_8 rings, the main component of the liquid above the melting point.¹ This transition, which affects various macroscopic physical properties such as viscosity,² specific heat,³ and density,⁴ can be explained by a simple chemical equilibrium theory⁵ and has been viewed recently as a critical phenomenon.⁶ Below T_p the liquid is mainly made of S_8 rings and above T_p it becomes a mixture of S_8 rings and long S_x chains. This change should show up in the structure of the liquid through the pair correlation function, $g(r)$, mainly at the distances corresponding to the third and fourth neighbors. In order to see such an effect we have performed neutron diffraction measurements as a function of temperature. We chose only two temperatures (130 and 150°C) below T_p , where no change is supposed to occur in the liquid structure, and four more temperatures above T_p where the liquid structure is expected to vary when the temperature rises, with more rings being polymerized into chains of decreasing length.⁵

The sample consisted of 3.5 cm^3 (about 6 g) of 99.999% purity sulfur, provided by Aldrich. It has been melted in a vitreous silica container, 9.5 mm inner diam, 11.3 mm outer diam, and about 100 mm total height. The neutron diffraction measurements have been performed on the hot source of the reactor Orphée at Saclay, using the $7C_2$ spectrometer described elsewhere,⁷ and with a 0.709 \AA wavelength [Cu(111) Bragg reflexion]. Diffraction spectra were collected by a 640 cells position sensitive detector covering an angular range of 128° in steps of 0.2° , which corresponds to a momentum transfer range from 0.4 to 16 \AA^{-1} . The furnace consisted of a vertical cylinder of vanadium, 30 mm diam, 0.1 mm thickness, and 300 mm height. The temperature gradient between the higher and lower parts of the silica container has been checked to be lower than 2°C at all temperatures. Conventional corrections have been applied to the raw data in order to take into account the effect of transmission, multiple scattering, and inelasticity. A vanadium probe

has been used to calibrate the 640 cells of the detector with a relative precision better than 0.1%. The low scattering length of sulfur (0.28 b) led to very long counting times (typically 36 h to get a statistical spreading of about 0.2% on the raw data). However, such a small scattering length minimized both absorption corrections and multiple scattering. The latter was less than 1% of the primary scattering, and thus assumed to be isotropic without significant error. The determination of the limiting value of the scattered intensity at low angle is crucial for the normalization of the structure factor. It is proportional to the isothermal compressibility; we checked that it exhibits large changes with temperature in agreement with previous thermodynamic measurements.¹

The structure factor $S(q)$ of liquid sulfur has been represented in Fig. 1 as a function of the temperature. It exhibits only very small changes for momentum transfer values higher than 3 \AA^{-1} thus suggesting already that very short range order is not changed in the whole temperature range. The main changes occur at smaller q ; the intensity of the first peak decreases from 1.25 at 130°C down to 0.95 at 300°C . The prepeak which can be observed at about 1.3 \AA^{-1} broadens and finally almost collapses into the main peak. As discussed above, the limiting value of the structure factor for q going to zero increases with temperature. Going to real space, the evolution of the pair correlation function $g(r)$ has been reported in Fig. 2. The very weak changes observed for $r < 4 \text{ \AA}$ correspond to the unchanged structure factor at large q . First- and second-neighbor distributions remain almost unchanged at all temperatures. No structure is detectable, within experimental uncertainties, for distances higher than 5 \AA . The most important changes on $g(r)$ occur between 4 and 5 \AA in the range of distances corresponding to the third- and fourth-neighbor distribution. In order to make these changes clearer we give an enlargement of this area. The peak decreases very slowly with temperature between 130 and 150°C but for higher temperatures the main maximum decreases rapidly from 1.35 down to 1.15 while the left side shoulder at about 4.2

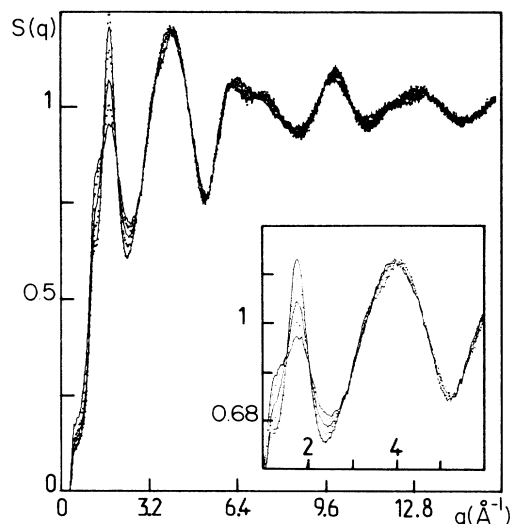


FIG. 1. The interference function $S(q)$ of liquid sulfur for the temperatures 130, 150, 170, 200, 250, and 300°C [the six functions $S(q)$ have been alternatively represented by dotted and solid lines]. An enlargement of the first two peaks is shown in the bottom right of the figure.

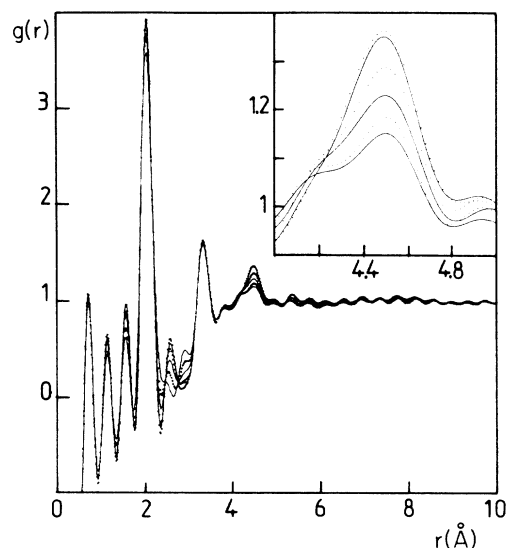


FIG. 2. The pair correlation function $g(r)$ of liquid sulfur for the temperatures 130, 150, 170, 200, 250, and 300°C [the six functions $g(r)$ have been alternatively represented by dotted and solid lines]. An enlargement of the third peak is shown in the top right of the figure.

Å decreases much more slowly, thus resulting in a broadening of the distribution of distances. Such an observation is already a qualitative evidence of local-order change expected to reflect the polymerization transition at the microscopic scale. In order to get this approach quantitative we have evaluated the coordination numbers corresponding to the first three peaks of the $g(r)$: n_1 , n_2 , and n_3 . Evaluation has been carried out by integrating between the minima around the peaks; in the case of the first peak where the $g(r)$ goes to zero for some temperatures, either $g(r)=0$ or $g(r)$ minimum has been used as the limiting value for the integration range. Results are given in Table I. All peak positions are very insensitive to the temperature increase. The corresponding coordination numbers for first and second neighbors are also almost constant whereas n_3 exhibits noticeable variations.

We first discuss the contribution of the first and second neighbors. As seen before, the distributions in distances are well defined and insensitive to the temperature. Therefore it can be assumed that the main feature of

liquid sulfur local order consists of a conservation of bond length and bond angle in the whole studied temperature range from 130 up to 300°C. Such a feature is very consistent with the strength of sulfur covalent bonding. Moreover, if we compare these distances to the distances in the orthorhombic structure of crystalline sulfur⁸ it should be noticed that bond length and bond angles exhibit in the liquid state almost the same value as in the crystal. If we want to compare our results to previous measurements, the only neutron experiment, to our knowledge, is the early work of Chamberlain.⁹ However, no systematic comparison can be done, as the structure was determined at only one temperature; therefore our data will be compared to x-ray diffraction results.^{10,11} A fair agreement can be found in the position of all peaks of the $g(r)$ and the differences in the first-neighbors number are small within the uncertainties of different methods of determination. But we quite disagree on the results on the second-neighbors number. In the first paper¹⁰ n_2 has been found equal to 4 at low temperatures with an abrupt

TABLE I. Peak positions r_i (in Å) and coordination numbers n_i for liquid sulfur as a function of temperature and for S_8 rings (Ref. 8).

T °C	r_1	r_2	r_3	n_1	n_2	n_3
130	2.056	3.35	4.51	1.86	3.12	7.52
150	2.050	3.34	4.50	1.85	3.07	7.41
170	2.049	3.33	4.50	1.85	3.05	7.18
200	2.048	3.33	4.49	1.84	3.04	6.96
250	2.045	3.33	4.50	1.86	3.00	6.66
300	2.042	3.34	4.50	1.90	2.92	6.45
S_8	2.044	3.31	4.43–4.68 4.51	2	2	2+1 3

decrease to 3 at 165°C. In the second one,¹¹ n_2 is of about 4 at low temperature slowly decreasing to 3.5 for higher temperatures. From crystallographic structure of orthorhombic solid sulfur⁸ we have calculated the distances between atomic positions and obtained the value $n_2=3$. It is thus difficult to explain the high x-ray value. Experiments are easier to perform with neutrons because of much less absorption, surface, and environment effects. Moreover, our machine allows to us reach higher values of q (16 Å⁻¹ instead of 12 Å⁻¹) and we are inclined to have more confidence in neutron than in x-ray scattering experiments. So the constancy of the values of n_2 in Table I confirms the conservation of both bond length and angle of liquid sulfur up to 300°C.

We shall now focus on the main structural effect directly linked to the polymerization transition and exhibited by the third coordination shell represented on the enlargement of Fig. 2. In order to follow on a quantitative level the structural evolution, we calculated the reduced coordination numbers n'_3 by integrating $g(r)-1$, to subtract from the usual coordination number n_3 the trivial contribution of the bulk density. Similar calculations have been done to determine for comparison the reduced coordination numbers n'_1 and n'_2 corresponding, respectively, to the first and second neighbors. All these quantities have been reported in Fig. 3 as functions of temperature. When the temperature increases, n'_1 and n'_2 show a slow monotonous decrease while n'_3 is strongly reduced from 1.11 at 130°C to 0.4 at 300°C. Moreover, the curve $n'_3(T)$ presents a discontinuity in slope around 160°C and most of the decrease takes place between 150 and 300°C. This behavior is consistent with the picture of a liquid made of S₈ rings only at low temperature and of a mixture of rings and random chains above the polymerization temperature T_p . We checked that the position of the third peak of $g(r)$ almost corresponds to the weighted mean of the third- and fourth-neighbor distances (two atoms at 4.43 Å and one atom at 4.68 Å) in an S₈ ring as deduced from the known structure of orthorhombic solid sulfur.⁸ This peak reflects local order of S₈ rings and shows very small variation below T_p . At the polymerization transition temperature, some S₈ rings start to break and recombine into long random chains in dynamic equilibrium with rings.^{5,6} The pair correlation function can then be considered in a simple approximation as a superposition of the pair correlation functions for rings and for chains, weighted, respectively, by the fractions of sulfur incorporated in rings Φ_R and in chains Φ_C ($\Phi_R + \Phi_C = 1$). In the region of the third peak of $g(r)$, the distribution of distances for a random chain is no more peaked at 4.43 and 4.68 Å but is a rather broad distribution between 3.3 and 6.7 Å. In consequence when the temperature increases from T_p , the rapid decrease of Φ_R from 1 (with the increase of Φ_C from zero) leads to the same variation of N'_3 which in a first approximation¹² is proportional to Φ_R , with $N'_3(T) = N'_3(130^\circ\text{C})\Phi_R$. The quantity Φ_R can be theoretically calculated^{5,6} and has been estimated experimentally as the weight fraction of

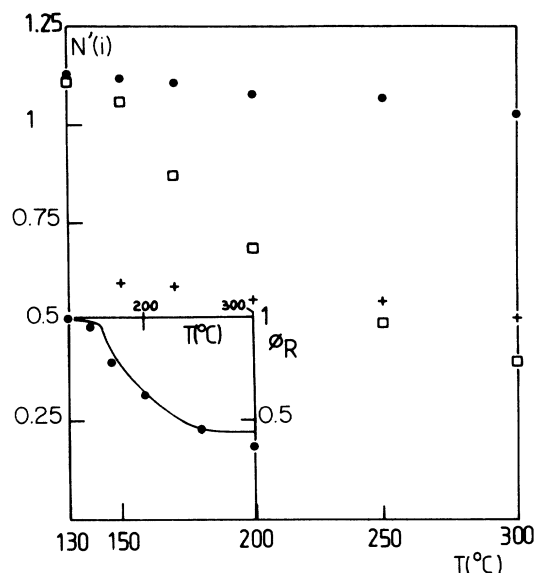


FIG. 3. Reduced coordination numbers n'_i ($i=1,2,3$) for the three first peaks of $g(r)$ in liquid sulfur as a function of temperature (n'_1 is represented by dots, n'_2 by crosses, and n'_3 by squares). In the bottom left of the figure we represented the mass fraction of sulfur in rings $\Phi_R^N = N'_3(T)/N'_3(130^\circ\text{C})$ for six different temperatures together with the weight fraction of soluble sulfur Φ_R^S (solid line) vs temperature obtained from Ref. 13.

sulfur soluble in CS₂ (Ref. 13) with the assumption that sulfur chains are insoluble and S₈ rings are soluble. Both $\Phi_R^N = N'_3(T)/N'_3(130^\circ\text{C})$ and Φ_R^S (the N and S superscripts are used to refer to Φ_R obtained, respectively, from neutron scattering and from solubility experiments) are represented in the inset of Fig. 3. A fairly good agreement can be observed and confirms that the thermal evolution of the $g(r)$ of liquid sulfur clearly exhibits the polymerization transition and therefore provides one with a description of this transition at a microscopic scale.

This thermal evolution of the $g(r)$ of liquid sulfur is also an experimental confirmation of a recent calculation¹⁴ by means of molecular dynamics. In contrast to our measurement, a higher distance for the third peak of $g(r)$ is predicted. However, the decrease of the peak with temperature due to the presence of the chains is well reproduced in the simulation.

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- ¹W. J. MacKnight and A. V. Tobolsky, in *Elemental Sulfur*, edited by B. Meyer (Wiley, New York, 1965), p. 95.
- ²R. F. Bacon and R. Fanelli, *J. Am. Chem. Soc.* **65**, 639 (1943); J. Ruiz-Garcia, E. M. Anderson, and S. C. Greer, *J. Phys. Chem.* **93**, 6980 (1989).
- ³F. Feher, G. P. Gorler, and H. D. Lutz, *Z. Anorg. Allg. Chem.* **382**, 135 (1971).
- ⁴H. Patel and L. B. Borst, *J. Chem. Phys.* **54**, 822 (1971).
- ⁵A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.* **81**, 780 (1959).
- ⁶J. C. Wheeler, S. J. Kennedy, and P. Pfeuty, *Phys. Rev. Lett.* **45**, 1748 (1980).
- ⁷J. P. Ambroise and R. Bellissent, *Rev. Phys. Appl.* **19**, 731 (1984).
- ⁸S. C. Abrahams, *Acta Crystallogr.* **14**, 311 (1961).
- ⁹O. Chamberlain, *Phys. Rev.* **77**, 305 (1950).
- ¹⁰C. W. Tompson and N. S. Gingrich, *J. Chem. Phys.* **31**, 1598 (1959).
- ¹¹K. S. Vahvaselka and J. M. Mags, *Phys. Scr.* **38**, 737 (1988).
- ¹²In this approximation we neglect two contributions acting in opposite directions: the very small contribution from the flat distribution of the chains proportional to Φ_C and an eventually small down trend of N_i^2 not linked to polymerization.
- ¹³J. C. Koh and W. Klement, Jr., *J. Phys. Chem.* **74**, 4280 (1970).
- ¹⁴F. H. Stillinger, T. A. Weber, and R. A. La Violette, *J. Chem. Phys.* **85**, 6460 (1986).