Crucial role of S_8 -rings in structural, relaxation, vibrational, and electronic properties of liquid sulfur close to the λ transition

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Crucial role of S_8 -rings in structural, relaxation, vibrational, and electronic properties of liquid sulfur close to the λ transition

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ABSTRACT

Liquid sulfur has been studied by density-functional based molecular dynamics simulations at different temperatures ranging from 400 up to 700 K across the well-documented λ transition. Structure models containing either a majority of S_n chains or S_8 rings are considered and compared to experimental data from x-ray scattering. The comparison suggests a liquid structure of a majority of twofold sulfur at low temperature, dominated by S_8 rings that open progressively upon temperature increase. Typical features associated with such rings are analyzed and indicate that they contribute to a specific third correlating distance in the pair correlation function and to a contribution at low wavevector k in the reciprocal space. The vibrational properties of liquid sulfur are also considered and indicate a contribution at 60 meV that is associated with both chains and rings, albeit the latter lead to a more intense peak at this wavenumber. The underlying network structure also impacts the dynamic properties of the melts which display enhanced dynamic heterogeneities when S_8 rings are present. The analysis of the electronic Kohn–Sham energies shows insulating character with a gap of about ≈ 2.0 eV, albeit the presence of localized mid-gap states is acknowledged that can be associated, in part, with the presence of S_6 rings.

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I. INTRODUCTION

Despite its rather simple electronic structure, typical of elements at the top of the Periodic Table, the origin of various properties specific to sulfur remains very complicated and has challenged our understanding for many years.

The solid state contains a certain number of polymorphic phases (allotropes) displaying either stable cyclic or chain-like molecular structures.^{1–5} At ambient pressure, two thermodynamically stable forms of sulfur can exist: (1) orthorhombic sulfur (α -S) consisting of a periodic arrangement of cyclic S₈ rings that transforms into a slightly different arrangement,⁶ viz., (2) monoclinic sulfur (β -S) for 371 < T < T_m = 392 K,⁷ the melting temperature T_m being an increasing function of pressure.^{8,9} As a result, both volume and enthalpy variations are small across

the orthorhombic–monoclinic transition.^{10,11} High pressure transformations do exist as well, and these have been continuously documented up to very recently, such as an identified rhombohedral sulfur polymorph containing rings of smaller size (S_6) driven by the kinetic transformation (e.g., laser induced¹²) of α -S,^{13–17} also termed *Engel's sulfur* because of its early characterization in 1891 by Engel.¹⁸ Due to the light-induced sensibility of the S_8 - S_6 transformation, analysis from Raman spectroscopy has led to certain controversial results^{5,12,19,20} but the sequence of ring reduction is now clarified and involves an intermediate form consisting in polymeric sulfur.^{14,21} The subsequent experimentally determined phase diagram can be found in Ref. 14. Additional high pressure forms have been established (e.g., tetragonal S) either from experiments^{22–27} or from computer simulations,^{28–34} which indicate the existence of extended-network phases that have been revealed up to 212 GPa^{26} and display both metallic and superconducting character.

The liquid state of sulfur is also of important complexity due to the obvious presence of polymorphism and possible liquid-liquid transitions. These might be extensions of the underlying sequences of transformations observed in the solid state. While the presence of several molecular-polymer transitions or the presence of mixed phases is detected in select pressure-temperature ranges,¹⁴ the most spectacular transition, specific to sulfur and termed the λ transition, is actually observed at ambient conditions³⁵ and remains even under moderate chemical alloying.³⁶ Upon melting α – S, the liquid consists of a disordered arrangement of S8 rings that collapse at the temperature of $T_{\lambda} = 159^{\circ}\text{C} = 432$ K into a mixture of rings and chain-like structures, the latter being similar to those encountered in the isochemical selenium liquid³⁷ and indicating the initialization of a polymerization process. The λ transition involves a certain number of observed thermodynamic and dynamic anomalies such as a discontinuity of the specific heat³⁸ and an unexpected viscosity behavior,^{39,40} which manifests by an abrupt increase of $\eta(T)$ with growing temperature and a maximum at 187 °C, prior to exhibiting a more typical behavior of fluid substances, i.e., an increase in fluidity with temperature. A certain number of experimental and theoretical studies have characterized the λ transition. While no specific structural signature is found from x-ray scattering in the reciprocal space,⁴¹ Bellissent and co-workers^{42,43} have suggested that the third coordination sphere is mostly affected by the change of the liquid structure across the λ transition, the distances involved in the first coordination shell at 2.05 Å (i.e., the S-S bond distance) and the secondary coordination shell at 3.35 Å being nearly unchanged. This picture has been globally confirmed by other diffraction measurements,^{44,45} whereas Raman scattering has led to the characterization of the population of the S8 ring modes with temperature.^{12,46,47} For more details and techniques, we refer the reader to a relevant review.48

We finally mention that sulfur as an element shares with selenium the unique property to form a glass from its supercooled state. As the latter is found in the region of the λ transition, the structure of glassy sulfur depends substantially on the thermal history; so, the obtained underlying structure and the ratio between chains and S_8 rings clearly influence the value of the glass transition temperature T_g . Using calorimetric measurements of weakly modified sulfides (e.g., Ge–P–S), it was shown^{49,50} that for a pure S_n chain network, $T_g \simeq 100$ °C, whereas it should be about -50 °C for a glass dominated by S_8 rings, the latter value being compatible with early measurements of the glass transition temperature.⁵¹ These differences simply signal the salient features of polyamorphism, highlighting the fact that liquids with different structures will lead to glasses with different values of T_g .

The aim of this article is to investigate the structural, vibrational, electronic, and relaxation properties of sulfur melts with increasing temperature from first-principles molecular dynamics simulations. In addition to phenomenological models, 52,53 there has been some previous numerical work on select properties of liquid sulfur that we briefly review. The main focus has been on the polymerization of the S_8 molecules and the effect of temperature, which appears to be crucial. Classical molecular dynamics simulations⁵⁴ performed on system sizes of about 1000 atoms have shown that the emergence of such S_8 rings upon decrease in the temperature is

TABLE I. Calculated fraction of sulfur (in %) belonging to rings of size p for model- S_n
and model-S ₈ at different temperatures. A cutoff of 2.67 Å corresponding to the
minimum of the pair correlation function (Fig. 3, see below) has been used. These
data are compared to experimental determination of the S ₈ fraction from x-ray
diffraction (XRD ^{60,61}), high-performance liquid chromatography (HPLC ³), and Raman
scattering. ⁴⁶ An additional experimental comparison is provided below.

T (K)	<i>p</i> =	6	7	8	>10	Chain
450	Model-S _n	1.2	1.5		2.1	95.2
	Model-S ₈	11.4	6.3	52.1	3.9	26.3
	XRD ⁶⁰					30.0
	HPLC ³	0.9	4.9	68.8	0.8	19.9
	Raman ⁴⁶					28.3
570	Model-S _n	1.2	1.5			97.3
	Model-S ₈	9.3	6.5	52.3		31.9
	XRD ⁶⁰			50.1		
	XRD ⁶¹			55.0		
	HPLC ³	0.9	4.9	60.6	0.5	28.4
	Raman ⁴⁶					45.0
700	Model-S _n	1.2	1.4		8.2	89.2
	Model-S ₈	9.6	4.2	52.9		34.1
	XRD ⁶¹			55.0		
	HPLC (660 K) ³	0.9	4.1	56.3	0.6	33.9

largely driven by relaxation phenomena and transition states allowing for the conversion of rings into polymeric sulfur chains. Their onset may, therefore, not be available on typical simulation times. First-principles molecular dynamics calculations based on densityfunctional theory (DFT) have been used to predict the structure, vibrational spectrum, and dynamics of liquid sulfur.^{55–58} The structure at high temperatures and/or after photoexcitation⁵⁶ is found to consist of chains of varying lengths resulting from the breakup of the S₈ rings, with the coexistence of chains of distinct length also proposed.⁵⁹

In this paper, we examine a complete set of properties of liquid sulfur from first-principles molecular dynamics simulations. Different models (either dominated by a chain-like structure or by S_8 rings, see Table I) and temperatures are investigated. The results indicate that while the large momentum (k) region of the structure factor S(k) can be very well described by both models at any temperature, as anticipated, S_8 models exhibit an increased agreement at low k. A similar conclusion holds for real space properties (pair correlation function) and the presence of S_8 rings induces a typical peak at $\simeq 4.5$ Å that can be characterized from a neighbor distribution function analysis. The dynamics of the corresponding melts reveals that S_8 -rich melts display an increased diffusivity but with a dynamics that is strongly heterogeneous, the most mobile particles being located on ring structures.

II. COMPUTATIONAL DETAILS

In model- S_n , we have simulated sulfur by the Car–Parrinello molecular dynamics⁶² using an ensemble NVT with N = 480 atoms and periodic boundary conditions on a cubic simulation box with

densities recovering the experimental ones.⁴¹ The integration time step was 0.2418 fs. In the DFT-D2 scheme, the electronic structure was treated by a norm-conserving Goedecker pseudopotential with the exchange correlation functional PBE in the GGA approach.^{63–65} Here, spin-orbit coupling has not been considered although some paramagnetic effects are known to exist in liquid sulfur.⁶⁶ The wavefunctions were expanded at the Γ point of the supercell and the energy cutoff was set at 20 Ry, the fictitious electron mass being taken as 1000 a.u. Table II summarizes the temperatures and densities⁶⁷ taken into account in order to compare them with the available experimental data, such as the structure factor S(k) or the pair distribution function g(r).⁴¹ To obtain the sulfur systems at the desired temperatures and densities, random initial configurations were run at 2000 K prior to a reduction of temperature (1500, 1200 K for 10 ps on each stage) and the investigation at the target thermodynamic conditions. Trajectories for each temperature were collected for 35-45 ps to generate structural, dynamical, vibrational, and electronic properties. These structure models are termed "model- S_n " because they contain essentially a chain-like structure. Additional runs ("model-S₈") have been performed at select temperatures on a second set of systems having a large fraction of S₈ rings. These configurations with N = 321 atoms were obtained by selecting a cubic slab from crystalline α -S prior to a short relaxation at high temperature (2000 K, 1 fs) that led to a disordered structure but with rings being preserved given that their dissolution takes place on long times (Fig. 1). For the latter system, subsequent trajectories were accumulated over 25 ps periods, each at temperatures of 450, 570, and 700 K. The corresponding structures were analyzed and compared with the 450, 570, and 700 K equilibrated liquids of model- S_n . A primitive ring analysis⁶⁸ of the



FIG. 1. Atomic snapshot of the N = 321 atom liquid sulfur system (model- S_8) containing a large fraction of S_8 rings.

obtained trajectories indicates that both models (model- S_n and model- S_8) differ, indeed, by their fraction of S_8 rings (Table I), the latter containing also several S_6 rings that are found in the rhombohedral elementary cell of the relevant sulfur polymorph.

TABLE II. Experimental⁴¹ (first line per composition) and calculated properties from model- S_n (second line in brackets) and model- S_8 (third line in brackets) of the different liquid sulfur systems: temperature, experimental density⁶⁷ ρ_0 , measured positions k_1 and k_2 of the first two principal peaks of the total structure factors S(k), first and second neighbor peak positions r_1 and r_2 of the total pair correlation function g(r), minimum r_{min} of the pair correlation function g(r), and coordination number r_S using the minimum r_{min} of the g(r).

Temperature (K)	$\rho_0 \; (\text{\AA}^{-3})$	k_1 (Å ⁻¹)	k_2 (Å ⁻¹)	<i>r</i> ¹ (Å)	r ₂ (Å)	r_{min} (Å)	r_S
400	0.0335	1.65	4.08	2.06	3.39	2.71	2.1
		(1.68)	(3.88)	(2.06)	(3.38)	(2.79)	(2.0)
450	0.0329	1.77	4.05	2.01	3.31	2.70	2.1
		(1.65)	(3.83)	(2.06)	(3.38)	(2.72)	(2.0)
		(1.73)	(4.01)	(2.07)	(3.38)	(2.69)	(2.0)
510	0.0325	1.73	3.91	1.93	3.25	2.65	2.1
		(1.68)	(3.88)	(2.06)	(3.37)	(2.66)	(2.0)
570	0.0317	1.77	3.86	2.05	3.31	2.53	2.2
		(1.50)	(3.96)	(2.05)	(3.37)	(2.67)	(2.0)
		(1.76)	(3.96)	(2.07)	(3.40)	(2.67)	(2.0)
600	0.0313	1.75	3.88	2.05	3.33	2.53	
		(1.63)	(3.91)	(2.06)	(3.39)	(2.65)	(2.0)
700	0.0297	1.75	3.86	2.04	3.29	2.53	
		(1.41)	(3.93)	(2.05)	(3.38)	(2.71)	(2.0)
		(1.79)	(3.96)	(2.06)	(3.37)	(2.67)	(2.0)

III. RESULTS AND DISCUSSION

A. Structure: Reciprocal space properties

The calculated structure factors S(k) are represented in Fig. 2 for both models and compared with the available experimental data from x-ray diffraction^{41,44} at different temperatures. Here, we have used the Fourier transform of the obtained pair correlation function (described below),

$$S(k) = 1 + \rho_0 \int_0^\infty 4\pi r^2 [g(r) - 1] \frac{\sin(kr)}{kr} dr,$$
 (1)

where ρ_0 is the system density.⁴¹ We first note an overall agreement that manifests by the correct reproduction of the main features. A closer inspection indicates an excellent reproduction of the secondary peak at $\simeq 4.0$ Å⁻¹ for both models (including peak positions k_i , see Table II), whereas the amplitude of the broad ternary peak between $k_3 = 6.0$ and 8.0 Å⁻¹ is only reproduced for T < 570 K. At small wavevector k, however, large differences emerge between the experimental data and the calculated structure factor. Here, the structural features between model- S_n and model- S_8 appear to substantially impact the behavior of S(k). For models of liquid sulfur with a large fraction of S_8 rings, a typical peak is obtained from the calculated S(k) at $k_1 = 1.73-1.79$ Å⁻¹ depending on temperature





(Table II), consistently with experimental findings⁴¹ (1.75–1.77 $Å^{-1}$) but at variance with the chain model (S_n) that leads to a principal peak at lower wavevector (1.41–1.65 Å⁻¹). These features indicate that a typical length scale of distance $L \simeq 7.725/k_1 = 4.38$ Å builds up for S-S correlations if a large fraction of S_8 is present. Here, we relate the position *r* of a peak in real space to the position *k* of a corresponding peak in Fourier space by using the relation $k.r \simeq 7.725$, which identifies the location of the first maximum of the spherical Bessel function $j_0(kr)$.⁶⁹ Furthermore, the S₈-model also leads to a shoulder peak in S(k) at even smaller wavevector (1.5 Å⁻¹) as also detected from the experimental data. This peak can be unambiguously assigned to sulfur chain contributions given the profile of the structure factor of model- S_n , which displays the dominant peak at 1.41-1.65 Å⁻¹ (Table II). Such a double contribution was identified earlier⁴³ as the contribution arising from chains and from S₈ rings, respectively. The amplitude of the S8 contribution was found to decrease with temperature as the chain structures start to proliferate at high temperature. Here, the simulation of the S₈-model only leads to a progressive growth of the chain contribution at the largest temperature and produces a broad peak with two well-identified contributions (green curve at 700 K, Fig. 2): a first one at 1.39 $Å^{-1}$ (experimental tail at a similar k) and a second one at 1.79 $Å^{-1}$ (experimentally⁴¹ 1.75 Å⁻¹).

The reproduction of the structure factor is an important result since the previous simulations on liquid *S* did not lead to a consistent picture. Apart from minor discrepancies in the peak heights in the region 6.0–8.0 Å⁻¹ and the shape of the first maximum at 1.5–2.0 Å⁻¹, the *S*₈-model shows the best agreement with experiments reported to date, the reproduction being very good at the lowest temperature (450 K).

B. Real space properties 1. Pair distribution function

We now concentrate on the structure in real space. The pair distribution function g(r) represented in Fig. 3(a) provides a probability density of finding any two sulfur atoms at a given interatomic

bility density of finding any two sulfur atoms at a given interatomic distance *r*. Due to the usually limited momentum transfer range accessible experimentally ($k < k_{max}$), in order to be consistent with the experimental methodology the calculated g(r) have been convoluted by a normalized Gaussian distribution with a full-width at half-maximum $\propto k_{max}^{-1}$, with maximum wavevector $k_{max} = 20$ Å⁻¹. This allows for a direct and meaningful comparison with experimental results,^{41,44} as also emphasized in other simulation studies.^{70,71}

We first note that the reproduction of the first and second neighboring correlations is excellent for all considered temperatures (Table II) as both the positions r_1 and r_2 and amplitudes of the calculated principal peaks fully agree with the experimental data and the identified typical distances of 2.05 and 3.31 Å.⁷² The calculated main peak (S–S distance and also bond lengths characteristic of S₆ rings¹⁶) is found to be about 2.05–2.07 Å for both the models and is very close to the one determined experimentally⁴¹ (2.01–2.06 Å). A similar conclusion can be drawn for the secondary peak.

Both models now differ at the third correlation shell found at $r \simeq r_3 = 4.5$ Å, and it is not surprising that differences observed in S(k) at low momentum transfer *k* now reflect in the radial distribution functions at large distances,⁷³ typically r > 4.0 Å. A difference plot [Fig. 3(b)] between models (S_8) and (S_n) shows, indeed, that



FIG. 3. (a) Calculated pair correlation function g(r) of liquid sulfur in S_n (black curves) and S_8 (green curves) models, compared with experiments (red⁴¹ circles). (b) Difference $\Delta g(r)$ plot between model- S_n and model- S_8 at 450 K.

increased contributions are detected from S_8 ring structures for the principal peak (2.0 Å) and the one at r_3 . An inspection of atomic snapshots and, more specifically, of S_8 ring elements suggests three typical correlating distances (Fig. 4). While the first one [Fig. 4(a), 3.50–4.71 Å] can be found in both the models as part of a *S*–*S*–*S* chain or a ring fragment and leads to the observed secondary peak



FIG. 4. Typical S–S correlation distances involved in S_8 rings: (a) Second neighboring distance common to both S_n and S_8 models. Third (b) and fourth (c) neighboring distances typical of S_8 rings.

of g(r) [Fig. 3(a)], the two other distances appear to be specific to S_8 ring structures [Figs. 4(b) and 4(c)], clearly different from interchain correlating distances of model- S_n , and they lead to contributions at 4.15–5.23 and 4.34–4.80 Å that are visible at 450 and 570 K in the corresponding calculated pair correlation function. We furthermore identify those distances in model- S_8 as those giving rise to the typical (S_8) peak at $k_1 = 7.7/r_3 = 1.71$ Å⁻¹ in reciprocal space.

Not only is the calculated coordination number r_S close to experimental findings (2.01–2.05^{42,74}), but it also indicates a weak temperature dependence (Table II), similar to liquid Se⁷⁵ but at variance with Te.⁷⁶ It should be noted that the important structural modifications are essentially seen at lower temperature⁷⁴ with an important change in both principal peak positions and amplitudes of g(r) at the λ transition.

2. Neighbor distribution functions

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It is instructive to inquire the origin of the observed differences close to r_3 between both these models. We use neighbor distribution functions $n_j(r)$ (NDFs) for this purpose. A set of NDFs can be defined by fixing the neighbor number j (first, second, etc.), the sum of all NDFs yielding the pair correlation function g(r). Figure 5 shows the results for both models in the region 3.0-5.5 Å for 450 K, i.e., the temperature at which the simulated peak arising from the S_8 -model is the most visible [Fig. 3(a)]. Note that both models lead, as expected, to a set of two NDFs (j = 1, 2) in the first shell of coordination ($\simeq 2.05$ Å, not shown) and to three additional ones (j = 3, 4, 5) for the second shell at 3.2 Å (not shown). These contributions are rather well separated from the third shell of neighbors, which roughly starts with the sixth nearest neighbor of a central atom (blue curves, Fig. 5).

For loosely structured systems, the absence of a third correlation peak is associated⁷³ with a monotonic decrease of the NDF amplitudes with growing j as exemplified in Fig. 5(b) (broken



FIG. 5. Neighbor distribution functions in liquid sulfur (450 K) for model-S₈ (a) and model-S_n (b) in the third principal peak region (3.25–5.75 Å). Relevant NDFs are colored (see text for details).



FIG. 6. Fragment of a 450 K structure of liquid sulfur. The third shell of neighbors (j > 9-10) must involve correlations between rings and chains. The gray zone is defined by a radius of 4.75 Å.

curves). This situation turns out to be the case for model- S_n made of near 100% *S* chains (Table I). Conversely, it is realized that for model- S_8 the presence of a peak at $r_3 \simeq 4.5$ Å is linked with an increased number of neighbors in the range j = 10-13 [red curves, Fig. 5(a)] that must obviously result from the presence (52%) of the S_8 rings. While the typical distances involved within the rings [4.34–4.80 and 4.15–5.23 Å, Figs. 4(b) and 4(c)] concern a lower neighbor rank (typically j < 8), a slab over select atomic configurations (Fig. 6), furthermore, permits one to identify that in this j range (10–13), the typical distances in the range $4.0 \le r \le 5.0$ Å involve ring–chain correlations.

3. Negligible miscoordinations

The integration of the first peak of the pair correlation function has led to a global coordination number of $r_S = 2$ (Table II). Once the fraction of r-fold coordinated species is calculated, one notices that a "8-N" (octet) coordination rule is satisfied for all considered temperatures, and for both models (Table III). The population of defect coordinations such as one- and three-fold *S* appears, indeed, to be very small (1%–3%), the former being related to terminal sulfur atoms within chains. Their population does not seem to depend on the considered models although the *S*_n-model contains about 90%–95% sulfur atoms within chains (Table I). An inspection of the atomic snapshots indicates that for the latter, very long chains are present in the simulation box, which confirms the conclusion drawn from the calculated coordinations (Table III). The calculated bond lifetime is about 1 ps, and during the simulation (e.g., 25 ps at

TABLE III. Calculated fraction (in %) of one-, two-, and three-fold S atoms in liquid sulfur for model- S_n and model- S_8 . A cutoff of 2.67 Å has been used.

T(K)		1	2	3
450	Model-S _n	2.5	96.4	1.1
	Model-S ₈	2.8	96.4	0.8
570	Model-S _n	0.9	98.3	0.8
	Model-S ₈	2.1	97.5	0.4
700	Model-S _n	1.4	98.2	0.4
	Model-S ₈	2.2	97.1	0.6

570 K), these chains are not dramatically altered, i.e., bond switching leads to chain recombinations, which maintain, on average, their lengths but do not induce the swapping of atoms between rings and chains.

4. Ring statistics

The calculated ring statistics have been given earlier (Table II). The algorithm is mostly based on the King⁷⁷–Franzblau⁷⁸ shortest-path search to find rings containing a maximum of 20 atoms.

Table I indicates that the obtained model structure of liquid sulfur (S_n) quenched from high temperature does not contain rings at all as their fraction is less than 3%. Conversely, model- S_8 not only exhibits a large fraction of S_8 rings of about 50% but also contains S_6 rings that are known to represent another elementary motif typical of rhombohedral sulfur.¹³ We also find possible "defect" rings having p = 7 sulfur atoms which are found in the liquid as well.⁴⁸

In model- S_8 , the effect of temperature on the ring fraction appears weakly visible as, e.g., the S_8 ring fraction remains nearly constant over the considered temperature interval of 450 < T< 700 K but appears to be consistent with the experimental determination of the polymer fraction from XRD^{60,61} and Raman spectroscopy for the largest temperatures (570, 700 K). An inspection of the whole statistics (Fig. 7) indicates, indeed, that the most dramatic changes in the S_n and S_8 fraction are found in the region $T_{\lambda} < T < 500$ K, the enthalpy of ring-chain conversion being estimated⁷⁹ as 153 kJ mol⁻¹. For larger temperatures, the liquid is made of a near 1:1 mixture of S_8 rings and S_n chains/other rings, the fraction of chains converges to a value of about 40%–55%, the latter values being subject to methods of measurements. An experimental analysis of the principal peak amplitudes of the function S(k) leads



FIG. 7. Evolution of the S_n chain (red) and S_8 population (blue) as a function of temperature. Evaluation from the FPMD trajectories of the S_8 -model (filled circles) is compared to results from XRD (Koh and Klement,⁶⁰ Crapanzano⁶¹), HPLC (Steudel and Strauss⁸⁰), Raman spectroscopy (Andrikopoulos *et al.*⁴⁶), and sound velocity attenuation.⁸¹ Earlier data^{52,82} are not represented.



FIG. 8. Calculated bond angle distribution P(cos θ) for select temperatures and the S_n (black) and S₈ (red) models: (a) 450 K, (b) 570 K, and (c) 700 K.

to S_n populations that are larger (50%–55%, Fig. 7)^{60,61} but probably also contain the signature of rings with $p \neq 8$. The details of the ring population have been measured from high-performance liquid chromatography (HPLC) of liquid sulfur quenched at different target temperatures.^{48,80} These results appear more consistent with our simulations (Table I) for both chain and S_8 statistics as we found, e.g., at 700 K 34.1% and 55.0%, respectively, to be compared with the experimental estimate of 33.9% and 56.3%.⁸⁰ At this point, having in hand the results of model- S_n obtained from a progressive melt quench (i.e., absence of S_8 rings), it is probably useful to reemphasize the kinetic origin of the ring nucleation process with decreasing temperature.⁵⁴ We conjecture that the present simulation time (tens of picoseconds) does not permit to generate directly the ring formation from high temperature molecular dynamics.

5. Bond angles

Figure 8 now represents the *S*–*S*–*S* bond angle distribution of liquid sulfur at different temperatures. The bond angle distributions show a strong peak at 110° and a weaker contribution at 160–180°. Both gradually broaden as T increases from 450 K up to 700 K. We note that there are only weak differences between the S_8 -model and the S_n -model that arise from the fact that the involved triplets *S*–*S*–*S* do not substantially change between model structures dominated by rings or by chains. However, a slight difference is noticeable around 90° at the lowest temperature, which might, indeed, arise from the presence of an increased ring contribution in the S_8 -model.

IV. VIBRATIONAL DENSITY OF STATES

Figure 9 now represents the vibrational density of states (VDOS) calculated from the Fourier transform of the velocity-velocity autocorrelation function of both models at 450, 570, and 700 K.

For the lowest temperature, we can eventually compare the values to a reported experimental spectrum⁸³ accessed from inelastic neutron scattering. One can notice that the main features of the VDOS consist in a broad band between 0 and 40 meV made of two dominant contributions centered at 5 and 25 meV, the latter being also detected from experiment whereas the former has not



FIG. 9. Calculated vibrational density of states for different sulfur liquids at (a) 450 K, (b) 570 K, and (c) 700 K and the two considered models: S_n (filled gray) and S_8 (red curves). The blue curve is an experimental measurement from inelastic neutron scattering⁸³ (scale adapted in order to highlight the relevant vibrational bands at 20–40 and 60 meV). The green symbols correspond to an eigenfrequency analysis of an isolated S_8 molecule.

been measured but reflects usually a contribution from internal low energy deformation modes.⁸⁴ A systematic investigation of sulfurrich glasses⁵⁰ has recognized that typical low frequency modes are detected at 42 cm⁻¹ (5 meV) and arise from two sources: floppy modes associated with the twofold coordinated *S* atoms in rings and chains and soft modes associated with a domain structure of glasses made of nanometer-sized elastically stiff regions in which atoms are strongly bonded and move together as a unit against other domains.⁸⁵

The second main contribution of the VDOS (Fig. 9) is the dominant peak detected somewhat below 60 meV, the S_8 -rich structure leading to a more intense peak (red curves) with respect to S_n . The presence of this peak in both models and sensitivity to temperature change (from 450 to 700 K) are compatible with earlier assignments from Raman scattering. ^{50,86} Narrow modes at 461 cm⁻¹ (57.2 meV) and 474 cm⁻¹ (58.77 meV) have been, indeed, associated with S_n chains and S_8 rings, respectively. Additional modes⁸⁶ are detected at lower frequency for the S_8 ring, i.e., 151 cm⁻¹ (18 meV), 217 cm⁻¹ (26.9 meV), and 440 cm⁻¹ (54.6 meV), but these are barely detectable from the calculated VDOS.

To further decode vibrational properties, we have performed DFT calculations on the isolated S_8 rings, which is the dominant structural motif at low temperature. The harmonic frequencies were calculated on optimized structures using as starting configurations a ring structure extracted from the 450 K configuration. Corresponding harmonic frequencies are provided on top of Fig. 9(a). These concentrate on the frequency range (0–65 meV) where Raman and IR active modes are present.⁵⁰ These can be linked with the main VDOS bands obtained from the velocity autocorrelation

function, i.e., we find a group of modes at [0–10 meV], [18–32 meV], and [45–62 meV] that are associated with complex bending and stretching vibrations involving dihedral angular motions.

V. DYNAMICS AND RELAXATION

In order to investigate the dynamics of the liquids, we first calculate the mean square displacement $(msd) \langle r^2(t) \rangle$ of the sulfur atoms from the atomic trajectories of our simulations,

$$\langle r^{2}(t)\rangle = \frac{1}{N} \left\langle \sum_{i=1}^{N} \left| \mathbf{r}_{i}(t) - \mathbf{r}_{i}(0) \right|^{2} \right\rangle, \tag{2}$$

where $\mathbf{r}_i(t)$ is the coordinate of the *i*th sulfur particle at time *t* and *N* is the total number of particles.

A. Diffusivity

From the time dependence of the *msd* (not shown) at the different target temperatures, one can calculate in the long-time regime the sulfur diffusivity *D* from the Einstein relation $D = \langle r^2(t) \rangle / \delta t$; the corresponding diffusion coefficients are represented as function of temperature in Fig. 10(a). For model-*S_n*, results suggest a behavior



FIG. 10. (a) Calculated diffusion coefficient *D* with temperature for model-*S*_n (black circles) and model-*S*₈ (green circles), compared to other numerical data (red filled square⁵⁷) and experimental data (open circles⁸⁷). The λ transition is indicated at the relevant temperature (T_{λ}). Arrhenius fits (lines) are performed on the datasets (see text for activation energies). (b) Calculated self-part of the Van Hove correlation function $4\pi r^2 \mathcal{G}_s(r, t)$ of liquid sulfur at 450 K (black) and 700 K (red) for the two models (S_n) and (S_6) at t = 10 ps. The gray zone corresponds to the deviation induced by a non-Gaussian tail in the 450 K Van Hove (VH) function, shown for model- S_n only.

of Arrhenius-type $D = D_0 \exp[-E_A/k_BT]$ with an activation energy of $E_A = 13.3 \text{ kJ mol}^{-1}$ (0.14 eV), which is a value substantially lower than other estimates from FPMD in chalcogenides (1.1 eV for GeSe2⁸⁸ or 0.4-0.8 eV for Ge-Se⁸⁹). This signals an enhanced diffusion for sulfur melts with respect to these 3D covalent liquids. The same calculation for the select temperatures of model-S₈ leads to diffusivities that are found to be slightly larger but consistent with another numerical estimation of diffusivity,⁵⁷ albeit both models clearly overestimate atomic transport from experimental measurements.⁸⁷ The latter lead at high temperature to an activation energy of $E_A = 0.21$ eV, which is slightly larger than the one obtained from FPMD simulations. We conjecture that these discrepancies might result from the electronic scheme as diffusivities are known to be subject to the choice in the DFT exchange correlation function which can modify the degree of covalency of the chemical bonding⁹⁰ and alter the atomic displacements (and corresponding diffusivities).

B. Van Hove correlations

An additional evidence for an increased motion at long times in S_8 -rich liquids is provided by the Van Hove (VH) correlation functions probing in real space the distribution of distances over which the particle has moved during a given time *t*. This is conveniently quantified by the self-part of the VH correlation function defined as

$$\mathcal{G}_{s}(r,t) = \frac{1}{N} \left\{ \sum_{k=1}^{N} \delta(r - |\mathbf{r}_{k}(0) - \mathbf{r}_{k}(t)|) \right\},$$
(3)

where $\delta(r)$ is the Dirac function. This function $\mathcal{G}_s(r, t)$ is the probability density of finding an atom at time t knowing that this atom was at the origin (r = 0) at time t = 0. By probing the probability that an atom has moved by this distance r, one is, therefore, able to gather additional information about the dynamics of the sulfur atoms. Figure 10(b) shows the function $4\pi r^2 \mathcal{G}_s(r,t)$ for two select temperatures (450 and 700 K) and the two structure models. Note that because of the isotropic nature of the system, the angular integration can be performed, leading to the term $4\pi r^{2.91}$ For short times, $4\pi r^2 \mathcal{G}_s(r,t)$ reduces by definition [Eq. (3)] to the Dirac function.⁹² For increased time, however, the sulfur atoms experience larger distances, this feature being also obtained at fixed time but with increased temperature. Figure 10(b) now indicates that the increased atomic motion found in model-S₈, as also revealed on average by an increased diffusivity (panel a), induces atomic jumps that are about $\simeq 1$ Å larger than the distances typically involved in the diffusive regime of model- S_n (i.e., long distances, r > 3.0 Å). We furthermore note that the jump probability between the first and second neighboring shells ($\Delta r = r_2 - r_1 \simeq 1.3$ Å) during 10 ps is increased for the chain models at low temperature [see low *r*-part of $4\pi r^2 \mathcal{G}_s(r,t)$ in Fig. 10(b)], and it is increased to a lesser extent at larger temperature.

C. Non-Gaussian tail and dynamic heterogeneities

Another important characteristic that appears from Fig. 10(b) is the non-Gaussian distribution, which contrasts with what would be expected for an ordinary liquid when relaxation phenomena are negligible.⁹² Here, the VH function appears to be much wider at long distances/times [gray area, Fig. 10(b)] and departs from the ideal VH

form^{93,94} $\mathcal{G}_s(r,t) = (4\pi Dt)^{-3/2} \exp[-r^2/4Dt]$, which results from a standard Fickian diffusion typical of high temperature liquids. The obtained tail is actually the manifestation of a nontrivial collective atomic motion⁹⁵ that is driven by dynamic heterogeneities.

When both models are analyzed, we obtain a profile for dynamic heterogeneities that is very different between model-S₈ and model- S_n . Figure 11 represents a *msd* distribution f(msd) of the sulfur atoms after a fixed time (20 ps) at the lowest considered temperature (450 K) for both models. Results indicate that the chain model exhibits a rather peaked distribution at msd $\simeq 1.0$ Å² with a tail that extends up to $\langle r^2(t) \rangle \simeq 6 \text{ Å}^2$. This signals that most of the particles are essentially moving/vibrating within the first coordination shell as $msd < r_1^2$, the first correlating distance, and only a small fraction of atoms experience motions with increased spatial extensions. Usually, the picture of dynamics that emerges from such salient features is made of vibrations around well-defined positions followed by jumps once atoms have been able to escape from cages.⁹⁶ Conversely, model-S₈ displays a broad distribution of mean square displacements (1-12 Å²) that are indicative of an increased dynamic heterogeneity and highlights the fact that the relaxation at the atomic scale is strongly heterogeneous. In model-S₈, an inspection of the spatial distribution f(msd) of the calculated individual mean square displacements (snapshot, Fig. 11) shows that the most mobile sulfur atoms are found on the ring structures and lead to various collective motions within or without cyclic structures, the dynamics along chains being more reduced. Taken together, these results provide a strong indication that one has a distribution of relaxing events that vary with space and time and depend crucially on topology (rings, chains). This might underscore the central role of dynamic fluctuations in the rapid variation of viscosity as one approaches the λ transition. We recall that due to inherent



FIG. 11. Mean square displacement histogram f(msd) at 450 K after 20 ps motion for both models: S_n (black) and S_8 (gray shaded). Fragments of atomic snapshots are provided and colored according to the *msd* scale (see text for details).

computer time limitations, this transition cannot be probed from FPMD simulations.

D. Relaxation phenomena

We now investigate the relaxation behavior of the sulfur liquids by examining the intermediate scattering function.⁹⁶ From MD simulations, the self-intermediate scattering function $F_s(k, t)$ is

$$F_s(k,t) = \frac{1}{N} \sum_{j=1}^{N} \exp(i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))), \qquad (4)$$

which is also the Fourier transform of the VH correlation function defined previously [Eq. (3)].

In Fig. 12, we represent the temperature dependence of $F_s(k, t)$ for two compositions at a fixed wavevector k = 1.77 Å⁻¹ that corresponds to the position k_1 of the principal peak in the static structure factor S(k) (Table II). The salient features of $F_s(k, t)$ are comparable to those of other typical glass forming systems.^{89,97-99} At high temperatures (not shown), the relaxation process takes place in a single step Debye-like fashion, and $F_s(k, t)$ decays to zero within the picosecond timescale. We note that both 700 K liquids do not exhibit such a profile, which is an indication that the system is already in a supercooled state with a decay that is stretched exponential⁹⁶ of the form $\exp[-(t/\tau)^{\beta}]$. At the lowest temperature (450 K), the decay becomes even more complex, and for model- S_n , it displays a typical β -relaxation plateau¹⁰⁰ that is detected around 10 ps.

In order to extract additional information from Fig. 12 and, particularly, the relaxation time τ_{α} , we use the simple estimate $F_s(k, \tau_{\alpha}) = 1/e$, which is also used in the literature.^{97,98} The analysis on the relaxation times as a function of inverse temperature is summarized in the inset for both models and exhibits an Arrhenius behavior with activation energies given by $E_A = 0.11$ and 0.18 eV for model- S_8 and model- S_n , respectively. These values are close to those obtained from diffusivity, consistent with the fact that D scales as τ_{α}^{-1} .



FIG. 12. Calculated intermediate scattering function $F_s(k, t)$ for the S_n (broken curves) and S_8 models (solid curves) at different temperatures. The inset shows an Arrhenius plot of the calculated relaxation time τ_{α} for the S_n (black circles) and S_8 models (green circles).

VI. ELECTRONIC PROPERTIES

Finally, we have performed calculations of the electronic structure (electronic density of states, EDOS), and these are displayed in Fig. 13 for 450 K. Note that no particular difference emerges in the EDOS between 700 and 450 K, except a reduction of the Fermi energy as we find, e.g., for model- $S_8 E_F = 1.65$ and 1.23 eV at 450 and 700 K, respectively. We note a similar bandgap for both models, somewhat smaller than the experimental estimates (2.5 eV).¹⁰¹

The EDOS consists in a series of bands located at $-17 \le E - E_F \le -9$ eV, $-7 \le E - E_F \le -3$ eV, and $-2.5 \le E - E_F \le 0.0$ eV for the valence band (VB), in addition to a contribution for the conduction band (CB) at $E - E_F > 1.0$ eV. The overall form of the valence band of liquid sulfur can be understood in terms of a contribution of s-orbitals [Figs. 13(b) and 13(c)] at $-17 \le E - E_F \le -9$ eV, together with a double band structure close to the Fermi level dominated by the p-orbitals.

An addition analysis uses the inverse participation ratio (IPR, turquoise in Fig. 13) defined by

$$IPR = \frac{\int d\mathbf{r} |\Psi(\mathbf{r})|^4}{\left(\int d\mathbf{r} |\Psi(\mathbf{r})|^2\right)^2}$$
(5)

and measures the degree of localized orbitals as large values are usually indicative of localization around specific bonds, i.e., IPR \rightarrow 0 for a fully delocalized state (conductor) and IPR \rightarrow 1 for a pure state. A combined inspection of panel (b) and (c) for the s-band and (d) and (e) for the p-band indicates that model-S₈ displays an increased localization with IPR values that are significantly larger than those obtained for the chain model, this feature being especially true for the low energy bands ($E - E_F \leq -9$ eV). The same situation holds for the edges of the p-band, and one furthermore notices mid-gap states



FIG. 13. Calculated electronic density of states (curves) and inverse participation ratio (IPR, turquoise bars) of liquid (450 K) sulfur for both models: model- S_n (black) and model- S_8 (red). (a) Total EDOS. (b), (c) s-orbital contribution. (d), (e) p-orbital contribution. The y-scale for the IPR is the same in all panels.



FIG. 14. Calculated chain (black) and ring (blue) contribution to the electronic density of states (curves) and inverse participation ratio (IPR, orange bars) of liquid (450 K) sulfur in model- S_8 : (a) and (b) s bands, (c) and (d) p bands. The y-scale for the EDOS and the IPR is the same in all panels.

 $(E - E_F \simeq 0.5 \text{ eV})$ that involve a large electronic localization as also previously detected in amorphous semiconductors.^{102,103}

From a selection of configurations at the lowest temperature (450 K) of model- S_8 , we identify atoms belonging to rings (R) or to chains (Ch), and the projected wavefunctions $\Psi_i(\mathbf{r})$ (i = Ch, R) are



FIG. 15. Ring contribution to the electronic properties of liquid (450 K) sulfur in model- S_8 . (a) s-band contribution from S_6 (black), S_7 (red) and S_8 (orange) rings. The inset shows corresponding IPRs for the S_6 and S_8 population. (b) Same calculation for the p-band structure.

then sorted according to their topology. The results are represented in Figs. 14 and 15 and reveal that ring structures lead to wellidentified contributions in both s- and p-band structures [Figs. 14(b) and 14(d)].

The data for the rings (see statistics, Table I) show selected energy modes at -8.5, -10.4, -13.1, and -15.3 eV with dominant s-contributions from S_8 rings, certain rings (e.g., S_6 and S_8) leading to specific signatures at, e.g., $E - E_F \simeq -9.4$ eV. For the p-band structure, a similar conclusion can be drawn and contributions from S_6 and S_7 appear to be similar. The dominant motif (S_8) turns out to be more localized (insets of Fig. 15) with IPRs that are larger, covering the entire range of accessible Kohn–Sham energies, and display enhanced contributions close to the low energy p-band VB and CB tail. We, finally, acknowledge that the identified mid-gap states at $E - E_F \simeq 0.5$ eV [Fig. 13(e)] arise from both chain and ring structures [Figs. 14(c) and 14(d)], the latter being clearly associated with S_6 rings (inset of Fig. 15(b)].

VII. SUMMARY AND CONCLUSIONS

Here, we have provided a systematic study of first-principles molecular dynamics simulations of liquid sulfur at different temperatures using different structure models, most of them being located above the λ transition. This transition is unique in elemental liquids and signals the presence of a liquid–liquid transition with wellidentified structural elements, i.e., S_8 rings at low temperatures and in the glassy state and a progressive breakdown of such rings at $T > T_{\lambda}$, the typical transition temperature.

Our results clearly indicate that quenched systems from high temperature melts do not permit to obtain structure models (model- S_n) that are compatible with this picture. Instead, the lack of ring structures underscores the kinetic origin for their nucleation, the limited timescale of FPMD being the obvious roadblock for a direct generation of such medium range order. Instead, we have generated "artificial" systems starting from crystalline $\alpha - S$ whose elementary cell contains such ring motifs, prior to a high temperature-short time treatment that has preserved the rings but induced a disordered melt structure (model- S_8). The population of such rings (52%) in this model is found to be consistent with the experimental determination using various methods, albeit weakly depending on temperature.

Once investigated at different temperatures, results now have indicated an increased agreement for model-S₈, which is able to reproduce the typical structure functions at various length scales: pair correlation g(r) and structure factor S(k) to a lesser extent. While the characteristics (position, width, amplitude) of the first and secondary principal peaks of the former are reproduced with great accuracy for both the models, the third typical correlating distance found experimentally⁴¹ at $r \simeq r_3 = 4.5$ Å is only recovered for model- S_8 . The presence of ring structures tends to reduce with increasing temperature, which also indicates the progressive breakdown of S₈ rings at elevated temperatures. An analysis from neighbor distribution functions reveals that neighbors $11 \le j \le 14$ around a central sulfur are responsible for the presence of this typical peak. Similarly, the difference in medium range order leads to profound differences at low momentum transfer k between both models in the function S(k), the double peak structure⁴¹ in the region $k \simeq 2.0$ Å⁻¹ being only qualitatively reproduced.

Additional properties have been studied in detail, such as the vibrational density of states—which displays two typical features at 40.0 and 60.0 meV that arise from both chains and rings. The latter can be, furthermore, decoded from the vibrational analysis of isolated S_8 molecules. The dynamic properties indicate an overestimation of the diffusion constant that is found to be Arrhenius-like at elevated temperatures, whereas the anomalies usually observed at the T_{λ} transition have not been considered due to the limited timescale of computer simulation at low temperature. Similarly, the relaxation time toward equilibrium is also found to be of Arrhenius-type with activation energies that are similar to those determined from diffusivity. We have, finally, considered the electronic properties and have identified contributions from chains and rings on the s- and p-band structure of the EDOS.

With the overall modeling scheme being validated and successfully compared to experiments, it is certainly interesting to probe the effect of system pressure on these liquids in order to theoretically investigate the complex phase diagram of liquid sulfur in more detail.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

H. Flores-Ruiz: Formal analysis (equal); Investigation (equal). M. Micoulaut: Investigation (equal); Methodology (equal); Writing – original draft (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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