

Liquid–liquid transition and critical point in sulfur

Laura Henry, Mohamed Mezouar, Gaston Garbarino, David Sifré, Gunnar Weck, Frédéric Datchi

▶ To cite this version:

Laura Henry, Mohamed Mezouar, Gaston Garbarino, David Sifré, Gunnar Weck, et al.. Liquid–liquid transition and critical point in sulfur. Nature, 2020, 584 (7821), pp.382-386. 10.1038/s41586-020-2593-1 . hal-02954824

HAL Id: hal-02954824 https://hal.science/hal-02954824

Submitted on 27 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Liquid-liquid transition and critical point in sulfur

Laura Henry¹, Mohamed Mezouar^{1*}, Gaston Garbarino¹, David Sifré¹, Gunnar Weck² &
Frederic Datchi³

4 ¹European Synchrotron Radiation Facility (ESRF), 71, Avenue des Martyrs, Grenoble,

5 France

6 ²CEA, DAM, DIF, F-91297 Arpajon, France

7 ³Institut de Minéralogie, de Physique des Milieux Condensés et de Cosmochimie

8 (IMPMC), Sorbonne Université, CNRS UMR 7590, MNHN, 4 place Jussieu, F-75005

9 Paris, France

A liquid-liquid transition (LLT) is a peculiar phenomenon in which a single-10 11 component liquid transforms into another one via a first-order phase transition. Due 12 to their counterintuitive nature, LLTs have intrigued scientists for several years and 13 changed our perception of the liquid state. Such LLTs have been predicted from computer simulations of water^{1,2}, silicon³, carbon dioxide⁴, carbon⁵, hydrogen⁶ and 14 nitrogen⁷. Experimental evidence has been mostly found in supercooled, i.e. 15 metastable, liquids such as Y2O3-Al2O3 mixtures⁸, water⁹ and other molecular 16 liquids^{10,11,12}, but the LLT in supercooled liquids often occurs simultaneously with 17 18 crystallization, making it hard to separate the two phenomena¹³. A liquid-liquid 19 critical point (LLCP), similar to the gas-liquid critical point, has been predicted at 20 the end of the LLT line in some cases, but so far never experimentally observed for 21 any materials. This putative LLCP has for instance been invoked in the case of water 22 to understand its thermodynamic anomalies¹. Here we report combined in-situ 23 density measurements, x-ray diffraction and Raman scattering that provide direct 24 evidence for a first-order liquid-liquid transition and a liquid-liquid critical point in sulfur. The transformation manifests itself by a sharp density jump between the low 25

and high density liquids, and distinct features in the pair distribution function. A
non-monotonic variation of the density jump with temperature is observed, which
first increases on moving away from the critical point and then decreases. This
behavior is linked to competing effects of density and entropy in driving the
transition.

31 The pressure (P)-temperature (T) phase diagram of sulfur exhibits important 32 similarities with that of phosphorus which is to date the only element for which a direct 33 *in-situ* observation of a LLT has been unambiguously evidenced^{14,15,16}. The stable sulfur solids at room P, α - and β -sulfur^{17,18}, consist of S₈ molecules, while at high P-T, the stable 34 polymorph is a polymeric solid composed of helical chains¹⁹ At room P the molecular 35 character is conserved in the liquid upon melting at 388 K and up to 432 K where the so-36 called "lambda transition" (λ -T) occurs²⁰. The λ -T has been described as a "living" 37 38 polymerization transition²¹, reversible and incomplete (the polymer content reaches a 39 maximum of ~60% at the boiling point, T=718 K), where a fraction of the S_8 cyclic 40 molecules open up and coalesce into long polymeric chains or rings. It is associated with 41 a large increase in viscosity and an anomalous but not discontinuous density variation^{20,22}. For P above 5 GPa and T above 1000 K, several P-T domains with different thermal and 42 electrical properties have been proposed in liquid sulfur²³. An experimental study²⁴ 43 44 suggested the existence above 6 GPa of a purely polymeric liquid composed of long 45 chains below 1000 K, which split to shorter chains at higher temperature. Ab-initio molecular dynamics simulations²⁵ reproduced this chain breakage in the compressed 46 47 liquid but found no discontinuous change of density associated to this process. So far, no 48 *in-situ* structural or vibrational studies have been conducted in the pressure region below 49 3 GPa in the mixed molecular-polymeric liquid.

We performed *in-situ* x-ray absorption, x-ray diffraction and Raman scattering at the beamline ID27 of the European Synchrotron Radiation Facility (ESRF)²⁶ to probe the density, structure and dynamics evolution of liquid sulfur in the P-T domain 0-3 GPa, 300-1100 K (see Supplementary Information S1-S3 for methods). The P-T paths are represented in the experimental phase diagram of sulfur in Fig. 1.

55

56 Figure 1

57 Density measurements were obtained in the Paris-Edinburgh press along eight 58 isothermal (P1 to P8 in Fig. 1) and two isobaric pathways (P9 and P10). The accuracy of the density measured by this method is of the order of 1% (Supplementary Information 59 60 S1). XRD patterns of the sample were also collected at each P-T point to confirm that the 61 sample was fully molten. As shown in Fig. 2a, along isothermal pathways P1-P5 below 62 1000 K, we systematically observed a discontinuous jump in density over a very narrow 63 pressure domain of ~ 0.07 GPa, strongly suggesting the existence of a first-order phase 64 transition between a low (LDL) and a high density liquid (HDL). Discontinuous density 65 shifts were also observed upon varying the temperature at constant load along pathways 66 P9-P10 (Supplementary Figure S9). These density jumps were accompanied by sudden 67 changes in the structure factor S(Q) of the sulfur melt, as shown in Fig. 2b. This is 68 particularly apparent on the width and position of the first diffraction peak which abruptly 69 change at the transition. The density variation estimated from the measured S(Q) using 70 the methodology of Ref. [27] (see Supplementary Information S3) very well compares 71 with that derived from the x-ray absorption measurements (see inset of Fig. 2c), giving 72 an independent confirmation of the discontinuous density jump at the transition.

73 Fig. 2c presents x-ray radiographic images taken along a compression pathway at 74 980 K and pressures between 1.6 and 2.5 GPa. These images show that below (panel i) 75 and above (panel iv) the transition, the sample is homogeneous, while at the transition an 76 interface separating a "bubble" of HDL from the surrounding LDL appears (panels *ii* and 77 iii). As seen in the Supplementary video 1, the HDL bubble grows as the load is increased 78 until the sample is fully in the HDL phase. These observations provide a compelling 79 evidence of a coexistence of the LDL and HDL phases at the transition, and together with 80 the density and structure factor measurements, confirm the first-order nature of the liquid-81 liquid transition.

82 At 1090 K and 1100 K (pathways P7 and P8 in Fig. 1), we did not observe, within 83 uncertainties, any discontinuous shift of the density as a function of pressure thus 84 indicating the presence of a liquid-liquid critical point (LLCP). The LLCP was likely 85 crossed along the pathway P6 at ~2.15 GPa and 1035 K (indicated by a star in Fig. 2a) 86 where the density measurements show clear anomalies (see Supplementary Information 87 S2), while at lower and higher pressures along this isotherm, the density appears to 88 continuously vary with pressure. As shown in Fig. 2d, we observe a non-monotonic 89 evolution of the density discontinuity with temperature: starting from zero at the LLCP, 90 it first increases to reach a maximum of ~7.5% at about 750 K and then decreases.

91 Figure 2

Fig. 3a shows the pair distribution function (PDF) g(r) obtained by Fourier transform of the measured S(Q) at 5 selected points along the P8 pathway: A, B and C are in the LDL domain, while D and E are in the HDL domain, close to the LDL-HDL transition line (see Fig. 1). The LDL PDF at point A (0.11 GPa, 428 K) is very similar to those reported for the ambient-pressure molecular liquid below the lambda transition^{28,29}.

97 It displays three well-defined peaks at 2.05, 3.39(2) and 4.45(2) Å, in very good 98 agreement with the previous cited works. As shown in the latter, the third peak is a 99 fingerprint of the S₈ molecule since it occurs at the average distance of the third and fourth neighbors in a S_8 ring, as deduced from the structure of the molecular α -sulfur crystal. 100 101 When the temperature is increased in the LDL domain above the lambda transition (points 102 B at 0.17 GPa-442 K, and C at 0.36 GPa-487 K), the observed evolution is also very similar to that described in the literature for the ambient-pressure liquid²⁸. Namely, the 103 104 positions and intensities of the first and second-neighbor peaks are weakly affected, 105 whereas the third peak strongly reduces in intensity and becomes bi-modal. These 106 changes in the third/fourth neighbor distribution are a signature of the rapid increase of 107 polymer content and associated reduction of the S₈ content above the lambda transition. 108 Indeed, the peak at 4.45 Å, characteristic of S₈ molecules, reduces in intensity and a new 109 component at 4 Å appears and grows with temperature, originating from the formation of 110 long polymeric chains or rings. The similarities between the present PDF in the region from 4 to 5 Å and those reported by Bellissent et al.²⁸ from ambient-pressure neutron 111 112 diffraction can be appreciated from the comparison of the inset of Fig. 3a and Fig. 3b. We 113 note however that the new component in the ambient pressure PDF appears at a larger 114 distance, around 4.2 Å, which is likely due to the lower density of the ambient pressure 115 liquid.

116 **Figure 3**

117

We now come to the structural modifications in the PDF across the LDL-HDL transition. As seen in Fig. 3c and S15, no change, within uncertainties, occurs on the first and second peak positions, showing that the S-S bond length and the <S-S-S> angle are

121 the same as in the LDL. The most important modifications occur again in the third/fourth-122 neighbour distributions. The bi-modal shape of the third peak is maintained but the component at 4.45 Å is even more reduced, and the component located at 4 Å in the LDL 123 undergoes a sudden shift in position to 4.15 Å in the HDL. This shows that the local order 124 125 in the liquid changes at the transition, and further, suggests that the polymer content in 126 the HDL is larger than in the LDL. The latter point is confirmed by the comparison of the 127 Raman spectra measured in the LDL and HDL shown in Fig. 3d. In the HDL domain, we observe an intensity increase of the stretching mode at 460 cm⁻¹ assigned to the polymeric 128 129 chains³⁰, concomitant with a drop of the molecular bending mode at 152 cm⁻¹ and breathing mode at 220 cm⁻¹ of the S_8 molecule, attesting that the latter are residual in the 130 131 HDL region.

132 This work thus demonstrates that sulfur undergoes a first-order phase transition 133 between two thermodynamically stable liquids, with clear experimental evidence of a 134 sharp density increase and structural modifications. We stress that this LLT is distinct 135 from the long-known lambda transition, which is associated to second-order like changes in density^{20,22} and heat-capacity³¹. Furthermore, the lambda transition temperature slowly 136 decrease with pressure³² whereas for the present LLT, the transition temperature increases 137 138 with pressure (see also Supplementary Information S4). By virtue of the Clapeyron 139 equation, and since a positive jump of density occurs at the transition, this tells us that the 140 entropy of the HDL is smaller than that of the LDL, which contrasts with the entropy increase in the LDL at the lambda transition³³. The entropy reduction across the LLT may 141 142 be due in part to the increase in polymer content revealed by present experiments, and 143 associated reduction in the mixing entropy. But the observed changes in the PDF also 144 indicate that the local conformation of neighbor polymeric units is modified, certainly to

a more compact arrangement imposed by the density increase, leading to a reduction inthe conformation entropy as well.

147 The shape of the transition line and the presence of a critical point make this LLT 148 in sulfur strongly resemble the well-known liquid-gas transition (LGT). However, there 149 is an important difference, which is the non-monotonic variation of the density jump with 150 temperature of the LLT, which first increases from zero as the temperature is decreased 151 from the LLCP and then decreases, contrasting with the monotonic increase of density 152 along the LGT transition. Such a behavior was recently predicted by AIMD calculations 153 along the LLT line of phosphorus³⁴, from which the authors suggested that the order 154 parameter describing the LLT contains contributions from both the density and entropy, 155 and that at least at low temperatures, entropy governs the transition rather than density. 156 This is at odds with the LGT where density is the sole order parameter. A two-order 157 parameters model including density, on one hand, and a bond-order parameter describing 158 locally favoured structures, on the other hand, was also proposed by Murata and Tanaka¹³ 159 to explain the existence of LLTs. The putative LLT in water has also been described as 160 entropy-driven based on a model where water is considered as an "athermal solution" of 161 two molecular structures with different entropies and densities³⁵. We note however that 162 the present LLT in sulfur is different from that in water and phosphorus in the sense that 163 the transition line has a positive slope in sulfur but a negative one in water and 164 phosphorus. This may signal that sulfur belongs to a different class of LLT.

165 This work also provides the first, to the best of our knowledge, experimental 166 evidence for a critical point terminating the line of a LLT. Such a LLCP was proposed in 167 phosphorus at about 3500 K – 0.02 GPa³⁴, conditions which have not yet been achieved 168 by experiment. In supercooled liquid silicon, classical empirical calculations have

predicted a LLCP at negative pressures (-0.6 GPa, 1120 K)³⁶ but *ab-initio* calculations recently determined that the HDL and HDL-vapor spinodals form a continuous reentrant curve, making supecooled Si a critical point free system³⁷. In water, the existence of a LLCP has been conjectured by Poole in 1992 et al.¹ to explain the many anomalies in the thermodynamic properties such as the heat capacity, compressibility and thermal expansion coefficients, and evidence for this LLCP has been strongly searched for and debated ever since. The experimental observation of this hypothetical LLCP in water may well never be possible as it is located in the "no man's land", i.e. the P-T domain below the homogeneous nucleation temperature. Finally, a LLCP has also been predicted in simple molecular systems, such as H_2^6 and N_2^7 but their experimental observation remain extremely challenging. The LLCP in sulfur, being in a P-T range easily accessible by experiment, provides a unique opportunity for the study of critical phenomena associated to LLTs. We thus expect that the present work will spark a new interest in liquid-liquid transitions that will provide a solid basis for understanding the principles that govern LLTs in general. Future works should also focus on deciphering the microscopic processes at the origin of the LLT in sulfur.

193 **References**

- 194 1. Poole, P. H., Sciortino, F., Essmann, U. & Stanley, H. E. Phase behaviour of
 195 metastable water. Nature 360, 324–328 (1992).
- 196 2. Harrington, S., Zhang, R., Poole, P. H., Sciortino, F. & Stanley, H. E. Liquid-liquid
- 197 phase transition: Evidence from simulations. *Phys. Rev. Lett.* **78**, 2409–2412 (1997).
- 198 3. Sastry, S. & Angell, C. A. Liquid-liquid phase transition in supercooled silicon.
 199 *Nature Mater.* 2, 739-743 (2003).
- 4. Boates, B., Teweldeberhan, A. M., & Bonev, S. A. Stability of dense liquid carbon
 dioxide. *Proc. Natl. Acad. Sci. U. S. A.* 109, 14808–14812 (2012).
- 5. Glosli, J. N. & Ree, F. H. Liquid-liquid phase transformation in carbon. *Phys. Rev. Lett.* 82, 4659–4662 (1999).
- 6. Morales, M. A., Pierleoni, C., Schwegler, E. & Ceperley, D. M. Evidence for a
 first-order liquid-liquid transition in high-pressure hydrogen from ab initio
 simulations. *Proc. Natl. Acad. Sci. USA* **107**, 12799 (2010).
- 207 7. Boates, B. & Bonev, S. First-order liquid-liquid phase transition in compressed
 208 nitrogen. *Phys. Rev. Lett.* **102**, 015701 (2009).
- 8. Aasland, S. & McMillan, P. F. Density-driven liquid-liquid phase separation in the
 system Al2O3-Y2O3. *Nature* 369, 633-636 (1994).
- 9. Mishima, O. & Stanley, H. E. The relationship between liquid, supercooled and
 glassy water. *Nature* **396**, 329-335 (1998).
- 213 10. Woutersen, S., Ensing, B., Hilbers, M., Zhao, Z., Angell, C. A., A liquid-liquid
 214 transition in supercooled aqueous solution related to the HDA-LDA transition.
 215 Science 359, 1127 (2018).
- 11. Tanaka H., Hurita R. & Mataki H. PRL 92, Liquid-liquid transition in the
 molecular liquid triphenyl phosphite. Phys. Rev. Lett. 92, 025701-4 (2004).

218

219	12. Kurita, R. & Tanaka H. On the abundance and general nature of the liquid-liquid
220	phase transition in molecular systems. J. Phys. Condens. Matter 17, 293-302 (2005).
221	
222	13. Murata, K. & Tanaka, H. Microscopic identification of the order parameter
223	governing liquid-liquid transition in a molecular liquid. Proc. Natl. Acad. Sci. USA
224	112 , 5956 (2015).
225	
226	14. Katayama, Y., Mizutani, T., Utsumi, W., Shimomura, O., Yamakata, M. &
227	Funakoshi, K. A. First-order liquid-liquid phase transition in phosphorus. Nature,
228	403 , 170–173, (2000).
229	15. Monaco, G., Falconi, S., Crichton, W. A. & Mezouar, M. Nature of the first-order
230	phase transition in fluid phosphorus at high temperature and pressure, Phys. Rev. Lett.
231	90 , 255701 (2003).
232	16. Katayama, Y., Inamura, Y., Mizutani, T., Yamakata, M. , Utsumi, W. &
233	Shimomura, O. Macroscopic separation of dense fluid phase and liquid phase of
234	phosphorus. Science 306, 848-851 (2004).
235	17. Steudel, R. & Eckert, B. Solid sulfur allotropes. Top. Curr. Chem. 230, 1-79
236	(2003).
237	18. Templeton, L. K., Templeton, D. H. & Zalkin, A. Crystal-structure of monoclinic
238	sulfur. Inorg. Chem. 15, 1999–2001 (1976).
239	19. Crichton, W. A., Vaughan, G. B. M. & Mezouar, M. In situ structure solution of
240	helical sulfur at 3 GPa and 400C. Z. Kristallogr. 216, 417–419 (2001).
241	20. Sauer, G. E. & Borst, L. B. Lambda transition in liquid sulfur. Science 158, 1567
242	(1967).
243	21. Tobolsky, A. V. & Eisenberg, A. Equilibrium polymerization of sulfur. JACS 81,
244	780–782 (1959).
245	22. Zheng, K.M. & Greer, S.C. The density of liquid sulfur near the polymerization
246	temperature. J. Chem. Phys. 96, 2175 (1992).

- 247 23. Brazhkin, V. V., Popova, S. V. & Voloshin, R. N. Pressure-temperature phase
 248 diagram of molten elements: selenium, sulfur and iodine. *Physica B* 265, 64–71
 249 (1999).
- 24. Liu, L. Kono, Y., Kenney-Benson, C., Yang, W., Bi, Y., & Shen, G. Chain
 breakage in liquid sulfur at high pressures and high temperatures. *Phys. Rev. B* 89,
 174201 (2014).
- 253

254 25. Plašienka, D., Cifra, P. & Martoňák R. Structural transformation between long
255 and short-chain form of liquid sulfur from ab initio molecular dynamics. *J. Chem.*256 *Phys.* 142, 154502-512 (2015).

257 26. Mezouar, M. et al. Development of a new state-of-the-art beamline optimized for
258 monochromatic single-crystal and powder X-ray diffraction under extreme conditions
259 at the ESRF. J. Synchr. Rad. 12, 659-664(2005).

- 260 27. Eggert, J., Weck, G., Loubeyre, P. & Mezouar M. Quantitative structure factor
 261 and density measurements of high-pressure fluids in diamond anvil cells by X-ray
 262 diffraction: Argon and water. *Phys. Rev. B*, 65, 174105 (2002).
- 263 28. Bellissent, R., Descotes, L., Boué, F. & Pfeuty, P. Liquid sulfur: Local-order
 264 evidence of a polymerization transition. *Phys. Rev. B*, 41, 2135-2138, (1990).
- 265 29. Vahvaselka, K.S. & Mangs, J.M. X-Ray diffraction study of liquid sulfur. *Phys.*266 *Script.* 38, 737-741, (1988).
- 30. Kalampounias, A. G., Kastrissios, D. T. & Yannopoulos, S. N. Structure and
 vibrational modes of sulfur around the lambda-transition and the glass transition. *J. Non Cryst. Sol.* 326, 115–119 (2003).
- 270 31. Braune, H. & Moller, O. The specific heat of liquid sulfur. *Z. Naturforsch.* 9a,
 271 210-217 (1954).

273	32. Kuballa, M. & Schneider, G. Differential Thermal Analysis under High Pressure
274	I: Investigation of the Polymerisation of Liquid Sulfur. Berichte der
275	Bunsengesellschaft für physikalische Chemie 75, 513–516 (1971).
276	33. Steudel, R. Liquid sulfur. Top. Curr. Chem. 230, 81–134 (2003).
277	34. Zhao, G., Wang, H., Hu, D. M., Ding, M. C., Zhao, X. G. & Yan J. L. Anomalous
278	phase behavior of first-order fluid-liquid phase transition in phosphorus. J. Chem.
279	Phys. 147, 204501 (2017).
280	
281	35. Holten, V. & Anisimov, M.A. Entropy-driven liquid-liquid separation in
282	supercooled water. Sci. Rep. 2, 713 (2012).
283	36. Vasisht, V. V., Saw, S. & Sastry, S., Liquid-liquid critical point in supercooled
284	silicon. Nat. Phys. 7, 549-553 (2011).
285	37. Zhao, G., Yu, Y.J., Yan, J.L., Ding, M.C., Zhao, X.G. & Wang, H.Y. Phase
286	behavior of metastable liquid silicon at negative pressure: Ab initio molecular
287	dynamics. Phys. Rev. B 93, 140203 (2016).
288	
289	
290	
291	
292	
293	
294	
295	
296	

297 Figure Legends

298 Fig. 1. Phase diagram of sulfur around the liquid-liquid transition. P1 to P8: 299 isothermal pathways followed during the density measurements presented in Fig. 2. P1, 300 P2, P4 to P7 were made on compression while P3 (diamond symbols) and P7 (open black 301 circles) were made on decompression. For clarity, P7 and P8 are shown up to 3 GPa only. 302 P9 and P10 are isobaric pathways followed during the density measurements presented 303 in Fig. S9 (Supplementary Information S1). The letters A, B, C, D, E (blue filled triangles) 304 along path P11 indicate the P, T conditions of the selected XRD data in Fig. 3. I, II and 305 III are the P,T points of the Raman spectra presented in Fig. 3. The black dashed line is 306 the transition line between the low density liquid (LDL) domain (in yellow) and the high 307 density liquid (HDL) domain (in pink) that terminates at the critical point Cp (black solid 308 circle).

309 Fig. 2. First-order liquid-liquid transition in sulfur. a. Relative pressure variation of 310 the liquid density ρ/ρ_0 (ρ_0 : density of the lowest pressure point for each isotherm) 311 collected along seven isothermal pathways (P1, P2 and P4 to P8 in Fig. 1). For clarity, the density jump obtained on decompression along P3 and along the isothermal paths P9 312 313 and P10 are presented in the Extended Data Fig. 1 and 3. Main panel: at T below 1030 K, 314 a clear density jump is observed along all the isothermal paths. At ~1035 K, a density 315 anomaly is detected in the vicinity of the LLCP (see Extended Data Fig. 4). Above the 316 LLCP (inset panel), a continuous variation of the density is observed. b. Structure factors 317 S(Q) of liquid sulfur collected along the isothermal path P2 (T=650 K). The red arrow 318 emphasizes the shift of the first peak position of S(Q) at the LDL-HDL transition. The S(Q)'s collected on decompression at 740 K are shown in the Extended Data Fig. 2. The 319 320 variation of the density calculated from the associated Pair Distribution Function (PDF) 321 (black filled squares) is presented in the inset panel together with the one obtained from 322 the direct density measurements (red empty squares). c. X-ray radiography of liquid sulfur 323 across the LDL-HDL transition line at T=980 K and pressures between 1.6 and 2.5 GPa. *i:* Pure LDL, *ii and iii:* LDL-HDL coexistence, *iv*: Pure HDL. The yellow arrow indicates the LDL-HDL boundary. **d**. Temperature evolution of the density jump. The black and blue symbols correspond to the isothermal pathways (P1 to P8) and, the red symbols to the isobaric (P9 and P10) pathways. A maximum of 7.5 % is located at ~750 K.

328 Fig. 3. Local order in the low- and high-density liquid sulfur. a. The main panel 329 presents the pair distribution function g(r) of liquid sulfur at selected pressure and 330 temperature conditions along path P11 of Fig. 1. The letters A to E in parentheses refers 331 to the P,T conditions in Fig. 1 at which the measurements were performed. The curves 332 are vertically offset by 0.3 for clarity. The inset shows an enlargement of the PDF in the 333 region from 0.4 to 0.5 nm which contains contributions from third and fourth neighbours. 334 **b** shows an enlargement of the third peak of G(r) from the ambient-pressure neutron data 335 of Ref. 28 at 423 K, 473 K and 573 K (the curves were digitized from Fig. 2 of Ref. 28). 336 c presents the position of the second, third and fourth neighbours as a function of pressure, 337 as deduced from the peak positions of the PDF along the path P11. Panel d shows selected 338 Raman spectra of liquid sulfur collected at the P,T points I,II and III of Fig.1. I: LDL 339 below the λ -T. II: LDL above the λ -T. III: HDL.

340 Extended Data Figure Legends

341 Extended Data Fig 1. Density discontinuity at 740 K. Raw datasets of isothermal x-

342 ray absorption profiles I/I0 collected on decompression at 740 K. The black arrow

343 indicates the density jump. B. Resulting isothermal density curve of sulfur in red and

344 density variation of NaCl pressure standard in blue.

345 Extended Data Fig 2. Structure factors S(Q) of liquid sulfur collected on

346 decompression along the isothermal path T=740 K. The black arrow emphasizes the

347 shift of the first peak position of S(Q) at the HDL-LDL transition. The variation of the

348 density calculated from the associated Pair Distribution Function (PDF) (black filled

squares) is presented in the inset panel together with the one obtained from the directdensity measurements (red empty squares).

Extended data Fig 3. Isothermal density discontinuity. Density of liquid sulfur as a
function of temperature along isobaric paths P9 at 0.4 GPa (left panel) and P10 at 1.3 GPa
(right panel).

354 Extended Data Fig 4. Liquid-liquid critical point in sulfur. Panels a and b: X-ray

absorption profiles I/I0 in the horizontal and vertical directions in the vicinity of the

356 critical point. **Panels c and d**: Horizontal x-ray absorption profiles at temperatures

below (950 K) and above (1090K) the critical point. The red arrow in panel **c** indicates

358 the I/I0 discontinuity at the liquid-liquid transition. No I/I0 discontinuity is observed at

temperature above the critical point (panel **d**).

360

361 Methods

362 Methods are available in the Supplementary Information at https://XXX

363

364 Acknowledgments

365 The authors acknowledge the European Synchrotron Radiation Facility for provision of

366 synchrotron beamtime at the beamline ID27, the Agence Nationale de la Recherche for

367 financial support under Grant No. ANR 13-BS04-0015 (MOFLEX) and the company

368 Almax easy Lab for providing the diamond cylinders.

369 Author contributions

- 370 The original idea was defined by MM. The experiments were performed by LH, GG,
- 371 DS and MM with equal contributions. The data were analysed and the figures produced

- 372 by LH with contributions from all the co-authors. The manuscript was written by MM
- and FD with contributions from all the co-authors.
- 374 Correspondence and requests for materials should be addressed to M. M.
- 375 (<u>mezouar@esrf.fr</u>).

376 Data Availability

- 377 Tables containing the data points for all the main and extended data figures are provided
- 378 as Excel files. The data that support the findings of this study are available from the
- 379 corresponding author upon request.

380 **Competing interests**

381 The authors declare no competing interests.





