

## Liquid-liquid transitions in molecular liquids: the cases of sulfur and phosphorus

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Keywords: Sulfur, phosphorus, liquid-liquid phase transition, critical point, x-ray diffraction, x-ray absorption

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First-order phase transitions separating two liquid phases of the same pure and isotropic substance has attracted considerable interest and research activity in recent years. About 20 years ago, such a liquid-liquid transition was discovered in elemental phosphorus by Y. Katayama and collaborators [1], which has had a large impact in the scientific community as it changed the way the liquid state was perceived. Since then, there has been experimental evidence for other liquid-liquid transitions in some supercooled liquids, but, despite intensive experimental research, no example of such transitions between two thermodynamically stable liquid states has been unambiguously found in any other substance than in phosphorus. Meanwhile, the existence of a liquid-liquid critical point (LLCP) terminating the liquid-liquid transition line has been widely debated and searched for in important systems such as water to explain its many thermodynamic anomalies, but has never been directly observed by experiment in water or any other system so far.

In this presentation, we will report on robust experimental evidence for a liquid-liquid transition and critical point in sulfur at high pressure and high temperature. Using several state-of-the-art x-ray based methods, we unambiguously demonstrate the first-order character of the transition, quantify the density discontinuity along the transition line, and characterize the differences between the two liquid forms at the atomic level. Our thorough investigation of the phase diagram in the 0-3 GPa, 300-1100 K domain enabled us to locate the transition line and demonstrate that it ends at a critical point. This thus constitutes the first

experimental evidence of the existence of a LLCP in any system so far. The latter being in a P-T range easily accessible by experiment, provides a unique opportunity for the study of critical phenomena associated to LLTs and has thus a general value beyond the specific sulfur system. Moreover, while we find common characteristics between the LLT in sulfur and that in phosphorus, the two differs in the sign of the Clapeyron slope which could indicate that the LLT in sulfur belong to a different class never observed before.

We also re-examined the nature and origin of the first-order LLT in phosphorus. We confirm that the transformation involves an abrupt density jump between two structurally distinct liquids and is associated to a drastic change of the viscosity. We accurately measured the temperature dependence of the density jump which exhibits a non-monotonic variation. As in sulfur, this is explained by competing effects of entropy and density, as the order parameter for the transition includes both contributions.

**Acknowledgments:** The authors acknowledge the European Synchrotron Radiation Facility for provision of synchrotron beamtime at the beamline ID27, the Agence Nationale de la Recherche for financial support under Grant No. ANR 13-BS04-0015 (MOFLEX) and the company Almax easy Lab for providing the diamond cylinders.

[1] Y. Katayama et al., Nature 2000, **403**, 170