

'Physique et Chimie des Matériaux' – ED 397 – année 2022

PhD project for funding, to send by 28/02/2022 to

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Research unit (full name + acronym) : Institut de Minéralogie, de Physique des Matériaux et de
Team if applicable : PHYSIX

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Project leader (PI): A. Marco SAITTA HDR? yes Position : Lecturer SU

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Nber of PhD under supervision 1 Participation to supervisor training? no Year

Co-supervisor : Frédéric DATCHI HDR? yes Position : Researcher CNRS

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Research unit : IMPMC

International co-supervision ? No

Keyword 1 : Machine learning Keyword 2 : Liquid liquid phase transition

Keyword 3 : Exp data analysis Keyword 4 : Ab initio calculations

Select co-funding programme if applicable : select

Project title : Machine learning experimental and modeling approaches for exotic phases of matter

Project Description :

The liquid-liquid transition (LLT) is a rare and intriguing phenomenon in which a single-component liquid transforms into another one via a first-order transition. Due to their counterintuitive nature, LLTs have intrigued scientists for several years and challenged our perception of the liquid state, for which the notion of polymorphism was long considered impossible. LLTs have been predicted from computer simulations of several systems, and heavily debated in the case of water. So far though, experimental evidence remain scarce and often controversial as they mostly concern supercooled, i.e. metastable, liquids where the LLT occurs simultaneously with crystallization, making it hard to separate the two phenomena. A liquid-liquid critical point (LLCP), similar to the well-known gas-liquid critical point, has been predicted at the end of the LLT line in some cases, but until our recent work on sulfur [L. Henry et al, Nature 584 (2020)], never observed in any material. As illustrated in the phase diagram of Fig. 1, taken from the latter work, the LLCP in sulfur terminates a first-order transition line between a low-density liquid (LDL) phase and a high-density liquid (HDL) one. In the case of water, this putative LLCP has been invoked to understand the numerous thermodynamic anomalies of water in the supercooled regime, but we have recently shown, by theoretical calculations, that water does not exhibit a LLT [under review], possibly ending a 30-year long debate in the community.

Scientific objective

The main objective of this project is to significantly advance our understanding of liquid polymorphism and LLTs, and, by extension, of the liquid state itself, by providing accurate experimental data sets that will constitute a solid basis from which the systematics of LLT can be extracted, and eventually will aid the emergence of theories from which predictions can be made. So far indeed, our understanding of LLT remains quite primitive, and there is no theory able to predict whether a given system will exhibit a LLT. This is why the

known experimental realizations remain scarce and have been made rather accidentally. To reach our objective, we propose to study elemental sulfur and phosphorous, over a large range of P-T conditions (0-150 GPa, 300-3000 K) and combine x-ray and optical diagnostics with theoretical studies using state-of-the-art ab initio computer simulations and machine learning techniques that will provide information at the microscopic and thermodynamic levels. If time allows, other systems, representative of various types of liquids (network, molecular and metallic liquids), will also be investigated, in parallel with experiments.

We plan to develop those kind of theoretical studies in close collaboration with the experimental tasks, supported by the ANR LILI, whose PI is the co-supervisor of the present PhD project. More specifically, we plan to approach at first the LLT in sulfur and phosphorus. We envisage in particular to gain microscopic insight on the relevant structural mechanisms driving those transitions, and to accurately determine the transition lines and critical points. To this end, it is mandatory to preserve the ab initio level of description of the interatomic interactions. Size effects, however, can be extremely important, and an extensive sampling of the liquid-states configurational spaces is necessary to probe those spaces with statistical significance. This is the major bottleneck from the computational point of view, which will require the development and use of specifically tailored machine-learning-based tools, such as High Dimensional Neural Network Potentials (HDNNPs), in collaboration with J. Behler (Göttingen University), one of the founders of the method, and main developer of the RuNNer code, with whom we have established a fruitful collaboration, and the Gaussian-approximation potential (GAP) method.

The first part of the PhD project will be devoted to the development and training of HDNNPs capable to accurately describe the local and global environment of sulfur atoms in the LDL and HDL phases. In the follow-up we will thus study the LLT in sulfur along the P6 pathway, using the HDNNP and GAP potentials, and our in-house methodology for the efficient statistical sampling of high-dimensional configuration spaces. The current project will also be an ideal playground to implement AI methods capable to make the crucial operation of interpreting XRD data less user-dependent, and even provide an optimized version of the current algorithms. To this end, we will use as a test-set at first a simple model system (rare gas) with synthetic data, then on experimental data on liquid sulfur and phosphorous. This part will be supervised by the co-PI.

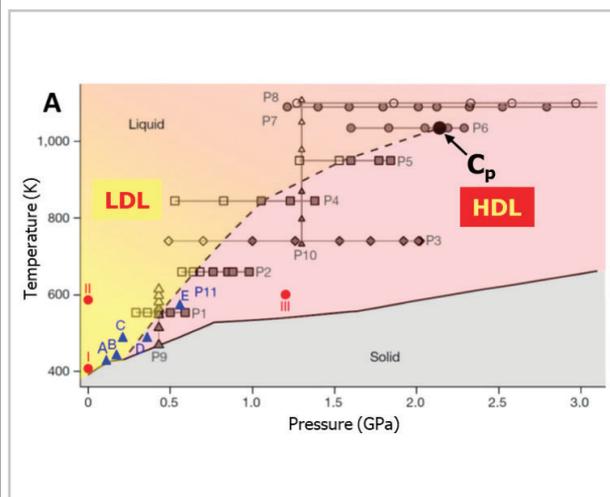


Fig. 1. Phase diagram of sulfur after [L. Henry et al, Nature 584 (2020)], in the P-T range of the liquid-liquid transition. P1-P11 indicate the various paths along which experimental measurements of density and structure were made.