PROGRAMME GRADUÉ ISAI

PSL UNIVERSITÉ PARIS

PhD Thesis offer

Academic year 2024-2025

PSL's ISAI graduate program is organizing a competition for a funded thesis.

The PhD student will be supervised by two researchers from two component institutions of PSL. Three subjects are proposed for this competition :

"Multiscale Modeling of Plasticity and Damage in Amorphous Solids: from atomistic computations to continuum mechanics"

PhD supervisors :

François Willot Centre de Morphologie Mathématique, Mines Paris -PSL

Sylvain Patinet Laboratoire de Physique et Mécanique des Milieux Hétérogènes (UMR7636) ESPCI - PSL

"Toward a " minimaly invasive " mechanical characterisation methodology of ancient metallic structures in view of their restoration or reuse"

PhD supervisors :

Anne-Françoise GOURGUES-LORENZON, Centre des Matériaux, Mines Paris -PSL

Matteo PORRINO, Laboratoire Géométrie Structure Architecture, ENSAPM - PSL

"Direct electrochemical conversion of ammonia in a high-temperature cell. Experimental approach and modelling"

PhD Supervisors :

Assaad ZOUGHAIB CEEP – Mines Paris- PSL

Virginie LAIR & Armelle RINGUEDE Armelle IRCP / I2E – Chimie ParisTech – PSL

The presentations of these PhD topics can be found below.

PhD candidates will send their applications to the holders of these projects, who will submit one candidate before 20 June 2024 to the board of the graduate program. Candidates will be invited to an audition at the end of June/beginning of July.. the thesis will be awarded to the candidate with the best academic record, motivation and suitability for the proposed subject

"Multiscale Modeling of Plasticity and Damage in Amorphous Solids: from atomistic computations to continuum mechanics"

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The deformation of amorphous materials at the continuum scale (>mm) is largely based on a phenomenological description of the mesoscopic scale (~µm). The present multidisciplinary PhD thesis, at the interface between physics and mechanics, aims to understand how atomistic simulations and micro-mechanical approaches may be combined in order to deal with plasticity and damage, and how a rigorous passage between the atomic and mesoscopic scales may be achieved. To do this, we rely on our recent methodological advances both at the atomic scale (ESPCI partner) and mesoscopic by FFT methods (Mines partner). This approach has already been validated in the case of simple loading and plasticity. We propose to extend this study to complex and more realistic cases (non-monotonic loadings and different fictitious temperatures) and to damage. For each protocol, mesoscopic and atomistic simulations will be compared quantitatively in order to identify the relevant parameters. The expected results will allow the derivation of physically justified behavior laws of amorphous materials.

Keewords :
atomistics, FTT, multi-scale, plasticity and damage

Problématique et objectifs scientifiques

Scientific issues and objectives

Although amorphous solids are ubiquitous in nature and have many industrial applications (glass, gel, granular materials), fundamental understanding of their mechanical behaviour is still limited. These disordered materials exhibit a universal mechanical response characterised by localised flow events that call for a global understanding. The crux of the problem stems from their disordered structure, which prevents the identification of topological flow defects, as is the case in crystals. At the particle scale, plasticity and damage occur through irreversible rearrangements. These shear transformations can aggregate as avalanches or form shear bands involving all spatial scales. Furthermore, the mechanical response of these non-equilibrium systems depends crucially on the details of the interactions between particles and their thermomechanical history.

Although continuous elasto-plastic models at larger scales successfully account for most phenomena, most of them are based on highly simplifying assumptions: scalar description, homogeneity of elastic and relaxation times, a priori threshold distributions, property statistics that do not change with plasticity and damage, and no pressure dependence. All these assumptions contradict the results obtained in recent years from microscopic simulations.

Given the softening character of most amorphous solids, which involves localisation, the classical homogenisation approaches used in mechanics should be avoided, and it is necessary to use kinematic models enriched with internal lengths. Some burning questions remain in this context: What is the microscopic origin of the non-

local rheology when moving from a discrete mesoscopic model to continuous approaches? How can internal lengths be physically derived?

On the other hand, while the fracture process is of immense importance, its understanding is still very limited. The modelling of fracture in amorphous solids coupled with plasticity and damage is rarely approached for amorphous heterogeneous systems. The reason for this is the great technical difficulty involved in dealing with the evolution of elastic heterogeneities and the nucleation of cracks associated with the appearance of elastic singularities.

It is in this context that the project leaders have recently developed innovative numerical techniques for : 1) systematically measure the local elastic limits of amorphous solids at the atomic scale, and 2) solve complete continuous mechanical problems (including plasticity and damage) in a heterogeneous solid using high-performance FFT methods. In this project, we propose to take advantage of these two new methodological advances to carry out rigorous multi-scale modelling of the mechanical behaviour of amorphous materials. The main thrusts of the project follow naturally from the opportunities offered by our respective areas of expertise. Firstly, we propose to transfer the information obtained at the atomic scale to discrete mesoscopic models capable of handling large systems, while focusing solely on the key parameters of the problem. Secondly, in order to validate our approach, we propose to quantitatively compare the atomistic and mesoscopic approaches as a function of the thermomechanical history of the material.

Approach and methods

We propose to extend this approach to the more realistic and complex cases of heterogeneous systems and non-monotonic loading. The first case is typically encountered for systems exhibiting localization. This phenomenon is generally associated with softening and the formation of shear bands that lead to material failure. Understanding this phenomenon is therefore essential for the design of new materials and structures. While this phenomenon has been reproduced using mesoscopic approaches, assuming an ad-hoc softening rule, it has not yet been studied on the basis of threshold evolution, which can now be measured directly at the atomic scale. A final challenge will be to implement a gradient (or phase field) damage model coupled to plasticity. We will be looking for a physical interpretation of the regularisation length introduced. The strategy will be to describe non-locality as the dependence of local stress diffusion on the rate of plastic events around the plastically deformed region.

Expected results - Challenges - Risks

In the best-case scenario, these lines of research will lead to a structural understanding of the mechanics of amorphous solids. In this case, the micromechanics of discretised instabilities would provide the basis for a physical theory of deformation. The project will also identify the key ingredients for a rigorous multi-scale approach. In a less optimistic scenario, we may find that the mechanical response of amorphous materials based on a continuous discretised description (even taking into account all the complexity as proposed here) cannot quantitatively reproduce the atomistic simulations. Even in this case, this work would provide numerous results by giving access to quantitative instability criterion statistics which, until now, have always been adjusted a posteriori at higher scales. This multi-scale strategy would also pave the way for the development of physically justified behaviour laws. In the longer term, it would provide a solid starting point for a less empirical design of new amorphous materials with controlled properties.

Contribution of the collaboration to achieving the objectives

At the interface between physics and mechanics, this project concerns several scientific communities. It brings together two laboratories from the ESPCI and the Mines, encouraging the emergence of inter-laboratory collaboration in the field of amorphous mechanics.

For the PMMH, it will strengthen approaches based on atomistic models of amorphous materials. The contribution of Mines' expertise is also essential for the mechanical aspects of continuous media: plasticity criteria, non-associated plasticity, multi-mechanisms, projection of mechanical fields.
This project would be an excellent starting point for a proposal for an ANR-type project that could aim to cover all scales up to the continuum. This is a particularly opportune moment for this project. Indeed, the project leaders have each spent the last few years developing new atomistic and continuous FFT simulation methods that make this innovative project of transfer between scales possible. This expertise is complementary and has never been pooled in this context. This thesis project will therefore enable us to reap the benefits of the long methodological developments that have already taken place.

“Toward a “ minimaly invasive ” mechanical characterisation methodology of ancient metallic structures in view of their restoration or reuse”

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The project, which stands on the interface between architecture and materials science, is exploring the characterisation of the mechanical strength of metallic structures of historical value. Resistance to deformation, i.e. flexural rigidity, can generally be measured using hardness evaluation, but resistance to fracture requires invasive tensile tests, which are not systematically conceivable on ancient structures. The aim of the project is to propose a methodology for characterisation by traction, based in particular on a choice of miniaturised specimen geometry that respects the characteristic lengths of the material and the validity of the tests. A study of the effects of scale and probabilistic modelling will enable the results to be linked to the relevant properties as part of the studies for the restoration/reuse of these structures.

Keywords:
Metal constructions, ferrous alloys, strength tests, historical heritage

Addressed questions and scientific objectives

A number of ferrous architectural structures that have been built since decades (or even centuries) are still currently in service. They constitute the most relevant research field to set up methodologies to be used for restoration/rehabilitation/refurbishment of metallic structures, whether or not being registered/listed and safeguarded as historical monuments.

New uses and contemporary requirements regarding safety and user comfort challenge any refurbishment project of these buildings. On the one hand, these structures were designed on the basis of less stringent safety requirements than today's, and are therefore sometimes found to be undersized. On the other hand, new architectural programs may involve loading conditions that were not anticipated at the time these structures were initially designed, for instance, increased traffic on bridges built in the 19th century and still in service.

Revisiting the resistance of these structures, using cutting-edge tools and approaches, would enable us to preserve these buildings and support any adaptation/transformation in the best possible conditions. This is the overall aim of this project, which straddles the boundary between architecture and materials science.

Tensile tests are used to characterize the mechanical properties of metals, including their ductility and their resistance to deformation and to fracture. For older metal structures (18th-20th centuries), this type of diagnosis enables residual strength to be estimated under very precise conditions. When it comes to characterizing older materials such as cast iron, puddled iron or certain rolled steels, these tests require substantial sampling of the structures, which is often difficult to accept in the interests of preserving their integrity.

High amounts of non destructive, easier-to-obtain *in situ hardness* measurements provide statistically representative values of the resistance to deformation, with little deleterious effect on structural integrity. Yet, converting hardness results into strength estimates is nowadays unsatisfactory. In particular, fracture properties cannot be evaluated from hardness properties, which limits the practical usefulness of these measurements.

This research project focuses beyond the correspondence between hardness and tensile strength values for ancient metals that contain a significant fraction of embrittling impurities.
More broadly, the project aims to define a methodology for investigating ancient structures that is minimally invasive (thus avoiding compromising the integrity of the existing structure) and as relevant as possible, for assessing the mechanical properties of parts and constructive elements, an essential prerequisite for the restoration and reuse of these structures.

Approach and methods

A multi-scale approach is selected for this project. It will start from historical metallurgy data on a few families of materials (including cast irons, puddled irons, and cast steels). The correlation between tensile data and hardness data will be studied. These measurements will then be associated to reference tests on subsized specimens. This will allow soundly supporting the relationships between deformation resistance (namely, hardness) and fracture resistance (tensile strength), while minimizing the impact on structural integrity. The underlying physical mechanisms are also to be elucidated. The subsized specimens are to be designed in view of the microstructure of these generally coarse-grained metals that contain a heterogeneous and anisotropic spatial distribution of non-metallic inclusions.
A similar approach is currently being used for modern structures (e.g. in-service monitoring of industrial plants, future use of pipelines for hydrogen transportation in the framework of the "MESSIAH" chair), as well as on model materials available in small quantities only (e.g. for the ANR JCJC "CAMEL" project). A strong novel aspect of the project is the application of this methodology to ancient materials.
The research work will also result in the definition of a multiscale characterization methodology. This methodology will address the transfer of results obtained on millimeter-sized specimens to the part or to the entire structure, e.g. using probabilistic modeling approaches.
The PhD student will start data collection and carry out studies at the structural scale (modeling and analysis of metal frameworks) at ENSAPM. The experimental program is to be carried out at the Centre des Matériaux (Mines Paris – PSL), with the help of the machining, mechanical characterization, and microstructural characterization platforms.

Expected results – Locks – Risk assessment and mitigation

The main aim of the research is to define and justify a "minimally invasive" investigation methodology of ancient structures, rigorously taking scale effects on tensile properties into account.
One of the locks to be solved is the design of subsized specimens, in particular, in view of characteristic length scales of microstructures to be tested, to carry out tests as representative as possible of real structures.
Right from the beginning of the research project, the availability of ancient materials for this project is to be secured. To this aim, colleagues and partners with whom M. Porrino is currently working, will be contacted, for instance, specialists of in situ hardness measurement on such structures (A-Corros company, Arles, France).

Interest of the collaboration to reach the objectives of the project

The GSA laboratory, in particular M. Porrino, is specialized in ancient metallic structures. He is highly experienced concerning their history, the materials that are

used, and the properties taken into account in their design. He will bring his scientific network for structural studies, as well as for providing of ancient materials. The research project will open the GSA laboratory toward mechanical tests dedicated to this kind of materials that are precious and hardly available to destructive characterizations. The PhD student will also face questioning about preservation and re-use of these structures. He/she is expected to work at the boundary between two scientific fields, namely, history of building and mechanical metallurgy.

The Centre des Matériaux will bring expertise in the characterization of deformation and fracture properties, either ductile or brittle, and including scale effects. A mixed experimental + modeling approach is to be used. The specific microstructures of these materials, inherited from ancient manufacturing processes well known to the GSA laboratory, are to be taken into account in the experimental program. The PhD student will use cutting-edge characterization of the links between microstructures of materials and fracture properties that is a core activity of the Centre des Matériaux. These methodologies are in fact relevant to any kind of material, so that the PhD student will enlarge his/her scientific skills in view of his/her future research carrier.

At the end of this project, the PhD student will be soundly trained to constructive typology and destination of ancient metallic structures in the architecture domain. He/she will also be soundly trained in mechanical metallurgy, in particular, in the design of advanced characterization methods. These skills are highly appreciated by the professional and industrial worlds, so that they will open a number of professional opportunities to the student at the end of the doctoral program.

"Direct electrochemical conversion of ammonia in a high-temperature cell. Experimental approach and modelling"

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Ammonia, as well as being a product already mastered by industry and being considered as a hydrogen carrier, has interesting energy density properties. For this reason, many studies have focused on the chemical cracking of the molecule at high temperatures (T > 400°C).
The study proposed here is to consider the conversion of ammonia directly in a molten carbonate fuel cell, of the MCFC type. The aim is to combine an experimental approach to electrochemical conversion with a modelling approach based on the Exergie Pinch methodology in order to optimise the operating parameters of the process while integrating thermal recovery.

Keewords :
Ammonia, fuel cells, modelling, cracking

Addressed questions and scientific objectives

The difficulty of storing and transporting hydrogen remains a major challenge in the hydrogen value chain. Ammonia (NH3) appears to be a promising material for storing and transporting hydrogen indirectly. Although its toxicity to humans is real and its production requires more virtuous approaches, it remains a flagship product of the chemical industry whose storage and transport, generally in liquid form (-33°C, 1 bar), appear to be controlled and safe [G. Jeerh et al, J. Mater. Chem. A, vol. 9, no. 2, p. 727, 2021]. Compared with compressed hydrogen (4.5 MJ/L at 700 bar and 25°C) and liquid hydrogen (8.49 MJ/L), liquid ammonia has a comparatively high volumetric energy density of 12.7 MJ/L.
While ammonia is an essential commodity on a global scale, mainly used in the production of nitrogen-based fertilisers, it can also be used as an energy carrier after cracking or directly in a fuel cell. Ammonia has a high heat of combustion (11 MJ/L) compared with liquid hydrogen (8.58 MJ/L), for example [M. Aziz et al, Energies, vol. 13, no. 12, p. 3062, 2020]. Cracking is generally used in industry for small-scale, local hydrogen production (2NH3 = 3H2 + N2). This process is carried out at atmospheric pressure, at a temperature of 800-1000°C, and requires a Ni-based catalyst. Temperatures can be lowered by using other catalysts based on iron, cobalt or ruthenium. In all cases, the catalysts are supported on oxides such as alumina, zirconia or ceria, and as the reaction is endothermic, the process is energy efficient [E. Spatolisano, : Ind. Eng. Chem. Res. 62, p10813, 2023].

The idea of this project is to study the use of ammonia fuel in a molten carbonate fuel cell (MCFC). When operating under state-of-the-art conditions, the materials used are nickel electrodes, an alkaline electrolyte based on lithium, sodium or potassium carbonates, and an alumina matrix, and the operating temperature is around 600°C.

The advantage of MCFCs is that they can be used directly with ammonia, as is envisaged in solid oxide batteries using ammonia. Nickel could act as a catalyst, even if the temperature is a little lower than in conventional processes, and the contribution of electrochemistry could compensate for the loss of energy in the form of heat. Also, the presence of alumina and alkali metals, which have been shown to decompose ammonia [H.S. Bamufleh, Processes, 11(8), p2287, 2023], would seem to be an advantage for this type of cell.
Furthermore, MCFC cells require the use of CO2, which can be reduced to CO or lead to the production of synthesis gas, by co-electrolysis of CO2 and water, also taking into account the reverse gas to water reaction (RWGS), [H. Meskine et al, IJHE, 46(28) p14944, 2021]. A recent study has shown that it is possible to produce synthesis gas using a chemical looping process, known as 'NH3-RWGS', from NH3 and CO2 [M. Keller, J. CO2 Utilization, 76, p102588, 2023].

The aim of this work is therefore, on the basis of recent results in the literature, to propose an innovative process for the direct conversion of ammonia in a molten carbonate fuel cell and to justify the energy recovery of the process by modelling.

Approach and methods

Firstly, a thermodynamic study will enable us to assess the possible reactions and the expected conversion rates, as a function of the working temperatures. This work can be carried out using HSC Chemistry software.

Electrochemical tests will be carried out in the laboratory, in batch, using various techniques (cyclic voltammetry, chrono techniques, etc.). Tests in complete MCFC-type cells will be carried out using state-of-the-art materials manufactured in the IRCP laboratory. Electrochemical measurements will be carried out, combining polarisation curves and electrochemical impedance spectroscopy. The inlet and outlet gases can be analysed operando, using the analysis techniques available in the laboratory, in particular gas chromatography and even mass spectrometry. Various experimental conditions could be tested (temperature, polarisation, flow rate and composition of the incoming gases, etc.) before considering the optimisation of certain electrode or matrix materials in order to improve conversion performance.

In parallel, using existing modelling in the ASPEN software developed at CEEP for an MCEC electrolyser, modelling can be carried out to simulate and optimise the conversion of ammonia in an MCFC cell. This process modelling will make it possible to use the Exergie Pinch methodology developed by CEEP to maximise the efficiency of the process. The Exergie Pinch methodology will simultaneously optimise the process operating parameters while thermally integrating the process. The introduction of thermodynamic exergy recovery systems will complete this optimisation. The results can be compared with more conventional processes, and a cost analysis can also be developed.

Interest of the collaboration to reach the objectives of the project

This project is innovative and exploratory in the sense that it aims to assess the possibility of using ammonia in a molten carbonate fuel cell and to couple the experimental results with process modelling (e.g. on Aspen Hysys), taking into account the energy and material balances throughout the process and assessing

the BOP (Balance of Plant).
The IRCP has experimental expertise in MCFC-type devices, with coupled analyses (GC-MS, FTIR, etc.), while the CEEP has expertise in the thermal and thermodynamics of energy systems, and in particular their simulation and modelling. CEEP has developed an original process optimisation methodology combining exergy analysis and the pinch-off method.

This project would enable the two teams to initiate collaboration, based on the complementary nature of their approaches. In addition, to our knowledge, this type of cell has not been the subject of any publications and the results could be enhanced by scientific production (article or even patent), if the performances obtained are encouraging.