ESF/Psi-K2 Workshop Scientific Report

Title: Materials Chemomechanics at the Atomic Scale: Modelling and Experiments

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Location: CECAM-HQ-EPFL, Lausanne, Switzerland

Organizers:
James Kermode (King's College London, UK)
Gianpietro Moras (Fraunhofer IWM, Freiburg, Germany)
Ralf Drautz (ICAMS, Bochum, Germany)
Alessandro De Vita (King's College London, UK)

Summary

Materials chemomechanics refers to complex interrelated chemical and mechanical processes that originate at the atomic scale and determine the mechanical behaviour of a material. An improved understanding of these processes is needed and has the potential for huge technological and economic impact. Our workshop brought together experimentalists and modellers to highlight the most relevant open problems and identify those which can be attacked by combining existing techniques.

Despite their enormous technological and economic importance, the nanoscale mechanisms underlying many chemo-mechanical processes in materials are still poorly understood. We believe this has in part a cultural origin: the training which chemists and solid state physicists have received in the last few decades is traditionally resonant of technologies like catalysis and semiconductor electronics, where mechanical properties are not immediately prominent. At the same time, the atomistic point of view has never been central in the training of mechanical or materials engineers, i.e. the experts who specialise in optimising the mechanical performance of structural materials. While this has recently started changing, the process of establishing a proper interdisciplinary tradition for atomistic modelling of chemomechanical phenomena is still in its infancy, in spite of its huge potential for impact and benefit to the modelling community's profile.

The problems which arise in chemomechanics are inherently multi-scale, which poses further, very distinctive technical difficulties. Describing chemo-mechanical phenomena requires algorithms which dynamically couple macroscopic stress fields with chemistry at the atomic scale, to reproduce experimental observations. This is difficult for three principal reasons. Firstly, the accuracy of quantum mechanical (QM) based techniques is needed in chemically active regions, but cannot be afforded in the entire simulated system. Non-uniform precision schemes involving the simultaneous coupling of QM and classical force field techniques can help address this issue, but the information efficiency of these techniques is still generally poor (e.g., most of the QM based information calculated is used just once during the simulation). Secondly, chemomechanical reactions typically take place on timescales longer than those accessible via

conventional molecular dynamics (MD), which requires rare events techniques to make significant progress. Thirdly, the experiments are themselves extremely challenging, because processes typically take place at buried defects or interfaces, hindering direct observation. As has become the rule in nanoscale science when complex chemistry is involved, fundamental theory is needed to guide and support experiment for producing new knowledge and significant progress. Indeed, in addition to presentations from modelling experts in various disciplines, feedback from key experimentalists therefore formed a key part of the workshop programme.

Scientific Content and Discussions

Thematic Overview Presentations

Peter Gumbsch kicked off the workshop by speaking about atomistic simulations of a number of chemomechanical problems of technological relevance: (i) hydrogen-induced stress corrosion cracking in silicon; (ii) stress-driven oxidation of silicon surfaces in wet environments; (iii) tribochemistry of carbon surfaces. Three different simulation approaches were used to tackle these problems. While full QM simulations were used for surface oxidation, a non-uniform precision QM/MM method (the “Learn on the Fly” (LOTF) technique) was necessary to tackle stress-corrosion cracking. The long simulation times required by tribological processes bring a need for reliable reactive interatomic potentials, with a hierarchical multiscale modelling approach to include chemistry. In all cases, the need for simple mesoscale models to scale the results to realistic timescales was emphasized. Continuing the scale-bridging theme, *Alan Cocks* spoke about scaling from micromechanics to the continuum level, including how the evolution of microstructure and the development of damage can be modelled. It was noted that chemistry can be included in hierarchical way, e.g. through diffusion constants.

At the end of the workshop, *Sidney Yip* wrapped up the contents of the previous discussions, emphasising once again the importance of developing mesoscale models. These are required to bridge the microscopic and the macroscopic scales. The mesoscale regime notably lies between technology “pull” and science “push” factors, leading to a hitherto somewhat underexplored “mesogap”. Three key examples of this were given: viscosity of glass, setting of cements, stress corrosion cracking.

Chemomechanics of Ductile Materials

Hydrogen embrittlement takes place in a number of metals which become brittle after exposure to hydrogen. For example, many modern high-strength steels have the potential for reducing the weight of cars significantly, but have found few applications because of their dramatic susceptibility to hydrogen embrittlement. *Oliver Rott* gave a description of current industrial research activities on hydrogen embrittlement, including both experiments and large scale modelling for high strength steels. He identified a “wishlist” of input that the steel industry would like to receive from atomic scale modelling, including diffusion barriers for H in steel and an improved understanding of the interaction between H transport, chemical reactivity and microstructure. From a theoretical perspective, *Jörg Neugebauer* presented a wide range of *ab*

initio thermodynamics calculations for H embrittlement, including the effects of entropy and anharmonicity, as well as classical interatomic calculations of interactions between dislocations/grain boundaries and H. Continuing this theme, *Bill Curtin* demonstrated a predictive parameter-free criteria for H-embrittlement of austenitic steels, based on diffusion-limited brittle fracture propagation. The model was developed from classical simulations that suggest the formation of hydride phases ahead of the crack tip, followed by brittle fracture propagation, providing that there is sufficient H diffusion towards the tip. *Afrooz Barnoush* described nanoindentation experiments, which he uses as a novel tool to understand H-embrittlement mechanisms. He demonstrated a simple continuum-based model in which hydrogen reduces the activation energy required to create a dislocation loop, which is compatible with his results. The discussion following his talk highlighted the scope for improved models based on atomistic simulations. Relatedly, *Tony Paxton* spoke about segregation embrittlement using thermodynamic models based on density functional theory (DFT) calculations of surface and segregation energies.

Other prominent chemomechanical processes relevant to the failure of ductile materials include the complex effects alloying has on material properties. *Alessandro Mottura* showed how Co-based alloys can be used as an alternative to Ni-based superalloys for gas turbine blades, with the same gamma/gamma prime phase mixture leading to high toughness. When constructing new alloys, there is a huge phase space due to the large number of possible combination of chemical elements, so there is a need for DFT calculations to calculate the stability of phases as a function of their composition, and for the development of simple rules to predict the effects of chemical composition on stacking fault energies.

Finally within the broad topic of ductile materials, *Laurent Proville* described quantum effects in thermally activated glide of dislocations in Fe, using classical interatomic potentials and the nudged elastic band (NEB) transition state method to calculate barriers, followed by quantum corrections to the zero point energy.

Simulation Methods

As noted in the summary above, chemomechanical processes are inherently multi-scale, leading to a requirement for advanced simulation methodologies. One session of the workshop was therefore devoted to novel techniques. *Jutta Rogal* presented applications of three variations of the kinetic Monte Carlo (KMC) technique for scaling up from atomistic calculations to reaction rates for rare events: (i) hydrogen diffusion; (ii) solid-solid phase transformation; (iii) solid-liquid phase transformation. *Matous Mrovec* explained how highly accurate bond-order potentials (BOPs) can be used as a bridge between electronic and atomic descriptions, following a rigorous route to derive the potentials from DFT with controllable approximations. He gave examples for magnetic bops for iron, Fe-H, and a number of other metallic systems. Somewhat relatedly, *Gabor Csanyi* described a functional-form-free, error-controlled scheme that can learn potential energy surfaces: the Gaussian Approximation potential (GAP). The main issue is obtaining an accurate representation of the local atomic environment. Applications to dislocations in W and brittle fracture of Si were presented. Finally, *Priya Vashishta* showed a

number of applications of reactive classical potentials in multimillion atom systems, all of which made use of petascale computing resources. Examples include the oxidation of Al nanoparticles and the formation and collision of gas bubbles in water. Finally, the application of divide-and-conquer DFT to a Al/water system, where controversies existed in the interpretation of experimental results, was presented.

Chemomechanics of Brittle Materials

One of the most important examples of chemomechanics in the context of failure and degradation processes in brittle materials is stress corrosion cracking, where cracks in ceramics and glasses exposed to a wet environment break under only very moderate (subcritical) loads. *Dov Sherman* described experiments and QM/MM (using the LOTF scheme) simulations of Si single crystal fracture in air and argon, demonstrating an environmental ("stress corrosion") effect for the first time. The impact possible only with a combined experimental/simulation approach to chemomechanical problems was highlighted during this talk. *James Kermode* described how brittle fracture can be modelled accurately at the atomic scale using a QM/MM technique (LOTF). Applications to crack-impurity scattering and low speed crack propagation via kink formation and diffusion were presented. From an experimental perspective, *Matteo Ciccotti* described slow crack propagation in oxides: using *in situ* nanoscale AFM measurements, he finds a ~2 nm large process zone, filled with water, ahead of the tip. A "wishlist" for input from modellers was presented, including the surface free energy of a glass, the molecular condition of water penetrating the glass, and the diffusion coefficient for water in glass and its dependence on stress.

Chemomechanics in Tribology

Chemomechanical processes taking place upon relative sliding of two surfaces have a huge influence on the tribological properties of materials, such as friction. *Jean-Michel Martin* described superlubricity mechanisms in a number of advanced tribological systems, including molybdenite crystals, hydrogenated amorphous carbon, tetrahedral amorphous carbon in contact with water and glycerol. Chemical mechanisms were investigated using a combination of several experimental tools and QM-based MD simulations. *Izabela Szlufarska* described simulations of ageing of silica contacts in aqueous environments: including chemical effects at the DFT level. She reported ageing is due to elastic-mediated interactions between siloxane bridges. The results are relevant for tribology of earthquakes, and consistent with AFM experiments. Izabela also showed the development of Green-Kubo relations for the efficient evaluation of friction/viscosity at solid/liquid interfaces. *Bernd Gotsmann* presented experimental evidence of atom-by-atom wear mechanisms in Si AFM tips in contact with hard polymers and ta-C. He made comparisons with theories and simulations, and also gave a wishlist for simulations, principally the ability to calculate "real" contact areas at the atomic scale.

Gianpietro Moras replaced *Michael Moseler* and spoke about the challenges modellers have to face when studying tribological systems of interest for industry. He identified the choice of model system as a key issue. Progress can be made using a hierarchical multiscale approach,

combining reactive potentials for mechanical wear, a QM description for surface reactions and non-reactive force fields for measuring friction coefficients for a given surface chemical termination. In chemically complex systems, where no reliable potentials are available, a QM/MM approach can be used to investigate local processes, e.g. for atom-by-atom reactions in silica/water systems.

Along similar lines to the topics described above, *Alex Shluger* described nanotribology simulations of water-mediated tip/surface contact in AFM. He also reported QM work on the diffusion of oxygen vacancies to grain boundaries in HfO_2, leading to electrical breakdown through percolation paths.

Summary of Key Discussions

In addition to the technical discussions mentioned above, there was consensus amongst all attendees of the need for time- and length-scale bridging techniques, and for two-way "wishlists" to be drawn up between the modelling and experimental communities. Participants also agreed on the need for accurate interatomic potentials, and/or hybrid/on-the-fly methodologies to reach larger scales and to tackle the transferability issues of such potentials. It became clear that despite many successful examples of collaboration between experimentalists and modellers, there is a difference of approach between the two parts of the community, and a need for improved knowledge transfer, which is something that could be addressed in future (see recommendations below).

Results and Impact of the Event

To our knowledge, this was the very first workshop run on the CECAM premises focussing on the modelling of chemomechanical processes. We see it as a seminal endeavour, which achieved the main goal of bringing together a community of researchers active in challenging research fields whose huge technological importance and present/potential impact on society is not yet reflected in the availability of advanced modelling tools (notably, at the atomistic scale and capable of QM-level accuracy). We brought together experimentalists and modellers working at various levels of theory to discuss possible ways towards systematic approaches to the study of chemomechanical processes in a variety of materials systems:

- Chemomechanics of ductile materials – e.g. hydrogen embrittlement, solution strengthening of metals, and fracture screened by plastic response.
- Chemomechanics of brittle materials – e.g. stress corrosion cracking of glasses.
- Tribochemistry – e.g. environmentally enhanced wear, superlubricity.

The most important advances required in this area over the next years are:

- Understanding atomic-scale mechanisms leading to modification of the mechanical

properties of metallic systems through chemical action, e.g. H-embrittlement, superalloy plasticity, segregation, solution strengthening.

- Understanding atomic-scale mechanisms for environment-dependent chemo-mechanical processes in brittle materials, e.g. stress corrosion cracking, wear and contact-ageing in AFM tips, lubrication of hard carbon coatings.
- Development of novel techniques: reactive interatomic potentials (e.g., Bond Order Potentials, Gaussian Approximation Potentials), non-uniform accuracy embedding schemes (e.g., Learn on the Fly, QM/MM), with the common goal of performing ”informationally efficient” simulations.
- Development of efficient approaches to scale-bridging, to transfer the knowledge gained from the understanding of these chemo-mechanical processes to larger scales, to make predictions at the experimental scale possible.

The requirement for an improved understanding of nanoscale experimental techniques by modellers, and of the capabilities and limitations of atomistic modelling by experimentalists, is common to all of these goals. This is mostly a problem of different backgrounds, and there is a need to build a common set of knowledge and a common vocabulary. We believe this is an area in which the modelling community may be able to make a valuable contribution, for example by hosting technical simulation workshops specifically designed for participants from experimental backgrounds interested in working more with modellers in future.

Future directions of the field, in particular those that might be funded by the EU 2020 programme include:

- Hydrogen embrittlement. This subject has already been funded during the FP7 programme and members of a funded Consortium were present at the workshop. This problem has an enormous economic impact and many industries are interested in basic research, both at the experimental and modelling level.
- Stress-corrosion cracking. Also in this case, despite its huge economic and technological relevance, little is known about the mechanisms leading to stress-corrosion cracking. In this workshop, the latest development in experiments and simulations of stress-corrosion cracking processes, together with possible links to wear of materials, were presented. There is scope for improved collaboration between state-of-the-art nanoscale measurements and atomic-scale simulations.
- Friction reduction. Stringent EU requirements concerning the reduction of CO_2 emissions, as well as the need for cost reduction, are driving industries towards new methods to minimize friction in mechanical systems. A precise knowledge of friction and lubrication mechanisms is still lacking and requires strong collaboration between experiments and modelling.
- Scale-bridging. In this workshop, the need for improved bridges between modelling and experiments at different scales has been highlighted. In particular, results gained at the atomic-scale should be used to feed larger mesoscale models in order to be able to compare to experimental scales and predict macroscopic behaviours of materials.

Future Impact on European Industry

The scientific scope of this workshop is strongly connected to applied research and to industry. The objective of the workshop was: “to bring together experimentalists and modellers working at various levels of theory to discuss possible ways forward, and to help establish new collaborations ... [with] a focus on scientific problems of ‘real’ contemporary industrial interest, by inviting R&D delegates from key EU industries.” Indeed, we received contributions both from leading EU industries and from EU research institutions that work actively with or for these industries.

The following are examples of areas where a better understanding of chemomechanical processes would lead to a direct impact for EU industry:

- Hydrogen embrittlement (steel companies, aerospace industry)
- Chemo-mechanics of superalloys (aerospace and energy industry)
- Fracture and stress corrosion cracking (oil, mining, glass and electronic industry)
- Friction and wear reduction (oil, automotive, electronics, lubricants)

Annex 1: Programme of the meeting

Day 1 - April, 29th 2013

- 13:30 to 14:00 - Registration
- 14:00 to 14:20 - Welcome

Afternoon Session (Chair: Izabela Szlufarska)

- 14:20 to 15:10 - **Peter Gumbsch** - Tribology and fracture processes: mechanics dominated by chemical reactions
- 15:10 to 16:00 - **Alan Cocks** - Micromechanics to continuum behaviour
- 16:00 to 16:30 - Coffee Break
- 16:30 to 17:20 - **Alex Shluger** - Electronic and ionic processes at solid interfaces
- 17:20 to 19:00 - Poster Session

Day 2 - April, 30th 2013

Morning Session (Chair: Gianpietro Moras)

- 09:00 to 09:50 - **Jean-Michel Martin -** Superlubricity: Quo Vadis?
- 09:50 to 10:40 - **Izabela Szlufarska** - Friction and Adhesion in Aqueous Environments
- 10:40 to 11:10 - Coffee Break
- 11:10 to 12:00 - **Bernd Gotsmann** - Nanoscale friction and wear from the point of view of individual atoms
- 12:00 to 12:50 - **Dov Sherman** - Chemisorption induced cleavage energy reduction in silicon crystal
- 12:50 to 14:30 - Lunch

Afternoon Session (Chair: Jutta Rogal)

- 14:30 to 15:20 - **Oliver Rott** - Simulations and experimental techniques to characterise the effects of hydrogen in advanced high strength steels
- 15:20 to 16:10 - **Jörg Neugebauer -** Understanding H-embrittlement in high-strength steels: An ab initio approach
- 16:10 to 16:40 - Coffee Break
- 16:40 to 17:30 - **William Curtin** - Nanoscale Mechanism of Hydrogen Embrittlement
- 17:30 to 19:30 - Poster Session

Day 3 - May, 1st 2013

Morning Session (Chair: Alessandro Mottura)

- 09:00 to 09:50 - **Tony Paxton** - Applications of density functional theory in segregation embrittlement
- 09:50 to 10:40 - **Afrooz Barnoush -** Hydrogen embrittelement revisited by novel nano-mechanical approach
- 10:40 to 11:10 - Coffee Break
- 11:10 to 12:00 - **Jutta Rogal** - Atomistic approaches for rare event systems
- 12:00 to 12:50 - **Priya Vashishta -** Reactive Nanosystems: Multimillion Atom Reactive Molecular Dynamics Simulations
- 12:50 to 14:30 - Lunch

Afternoon Session (Chair: Ralf Drautz)

- 14:30 to 15:20 - **Matous Mrovec** - Bond Order Potentials for Elements and Compounds: The Bridge between Quantum Mechanics of Electrons and Classical Mechanics of Atoms
- 15:20 to 16:10 - **Gabor Csanyi** - A news bulletin from the developing world of autogenerated interatomic potentials
- 16:10 to 16:40 - Coffee Break
- 16:40 to 17:10 - **Gianpietro Moras** – Challenges in the atomic simulation of wear processes
- 17:10 to 17:40 - **James Kermode** – Multiscale Simulation of Brittle Fracture in Oxides and Semiconductors
- 19:30 to 22:00 - Social Dinner

Day 4 - May, 2nd 2013

Morning Session (Chair: James Kermode)

- 09:00 to 09:50 - **Alessandro Mottura** - From Ni-based to Co-based superalloys: planar fault energies to order
- 09:50 to 10:40 - **Laurent Proville** - Quantum effect in thermally activated glide of dislocations
- 10:40 to 11:10 - Coffee Break
- 11:10 to 12:00 - **Matteo Ciccotti** - Multiscale investigation of slow crack propagation in glassy polymers
- 12:00 to 12:50 - **Sidney Yip** - On connecting glass viscosity, cement setting and stress corrosion cracking: Implications for materials modeling and simulation at the mesoscale

Annex 2: Full list of speakers and participants

Organizers

Alessandro DE VITA	United Kingdom, King's College London
Ralf DRAUTZ	Germany, Ruhr University, Bochum Status
James KERMODE	United Kingdom, King's College London
Gianpietro MORAS	Germany, Fraunhofer Institute for Mechanics of Materials

Speakers

Afrooz BARNOUSH	Norway, Norwegian University of Science and Technology
Matteo CICCOTTI	France, ESPCI, Paris
Alan COCKS	United Kingdom, University of Oxford
Gabor CSANYI	United Kingdom, University of Cambridge
William CURTIN	Switzerland, EPFL, Lausanne
Bernd GOTSMANN	Switzerland, IBM Research, Zurich
Peter GUMBSCH	Germany, University of Karlsruhe
Jean-Michel MARTIN	France, Ecole Centrale de Lyon
Michael MOSELER	Germany, Fraunhofer IWM
Alessandro MOTTURA	United Kingdom, University of Birmingham
Matous MROVEC	Germany, Fraunhofer IWM, Freiburg
Joerg NEUGEBAUER	Germany, Max-Planck Institute for Iron Research
Tony PAXTON	United Kingdom, National Physical Laboratory
Laurent PROVILLE	France, CEA-Saclay
Jutta ROGAL	Germany, ICAMS - Ruhr University Bochum
Oliver ROTT	Germany, ThyssenKrupp Steel Europe
Dov SHERMAN	Israel, Technion Israel Institute of Technology
Alex SHLUGER	United Kingdom, University College London
Izabela SZLUFARSKA	USA, University of Wisconsin - Madison
Priya VASHISHTA	USA, Uni Southern California
Sidney YIP	USA, Massachussetts Institute of Technology
Younsuk YUN	Switzerland, Paul Scherrer Institute

Other Participants

Federico BIANCHINI	United Kingdom, King's College London
Arsim BYTYQI	Slovenia, Institute of Metals and Technology
Marco CACCIN	United Kingdom, King's College London
Miroslav CAK	Germany, ICAMS, Ruhr Universität Bochum
Nermine CHAARI	France, CEA Saclay
Maria Isabel DE BARROS BOUCHET	France, Ecole Centrale de Lyon
Michael FRANCIS	Switzerland, EPFL
Chiara GATTINONI	United Kingdom, Imperial College London

Yeliz GüRDAL	Turkey, Koc University Chemical Society
Tilmann HICKEL	Germany, Max-Planck-Institute for Iron Research
Sathiskumar JOTHI	United Kingdom, Swansea University
Andreas KLEMENZ	Germany, Fraunhofer IWM, Freiburg
Zhenwei LI	United Kingdom, King's College London
Sebastian SCHREIBER	Germany, ICAMS, Ruhr-Uni Bochum