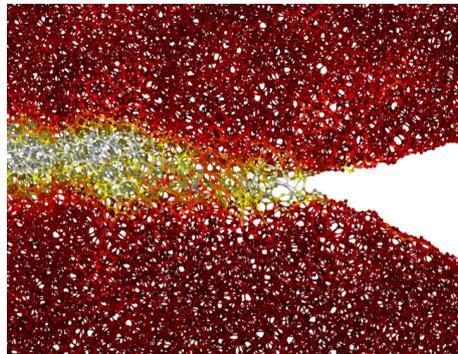


# Chemical and Structural Transformations in Materials under Mechanical Load



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**CECAM-HQ-EPFL, Lausanne, Switzerland**

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## Chemical and Structural Transformations in Materials under Mechanical Load

James Kermode, Lars Pastewka, Gianpietro Moras, Alessandro De Vita and Mike Payne  
Report on a workshop that took place at CECAM-HQ, Lausanne, 1st-4th September 2015

**State of the art.** Our current capability to model complex chemical-mechanical processes relevant for e.g., tribology, fracture and plasticity in ceramics, oxides and metals was clearly identified at the workshop. Key strengths that were identified include the accuracy of quantum-mechanical (QM) simulations of realistic systems with several chemical elements, usually based on density functional theory (DFT). In parallel, accurate and efficient classical interatomic potentials exist for many unary and binary metallic and covalent systems. Important steps forward have been made in the development of free energy methods and their application to important entropically driven materials problems. The link from DFT to classical atomistic simulations is well established but there is clear scope for further improvement e.g., though the automatic generation of reactive potentials for three or more elements. Obtaining mechanistic insight was identified as a key strength of modelling. There was a strong consensus that our main focus should remain here, rather than attempting the direct simulation of systems with the full complexity typically encountered in engineering applications. Cross-fertilization between adjacent fields with similar problems is important and common, and close collaboration of experimental and theoretical teams is very encouraging. The interoperability of data and codes has improved markedly in recent years. The emergence of shared datasets is expected to capitalise on this, helping to ensure less time is spent recalculating the same properties.

**Where the field is going.** Mechanical properties of materials, such as friction, wear, fracture, plasticity, toughness or yield strength are still theoretical challenges and deserve future attention, in particular for complex multicomponent systems in contact with environmental chemistry. The field is moving toward advanced sampling techniques to capture phase space (free energies) and predict, e.g. unbiased phase diagram without an *a priori* knowledge to truly identify phase-boundaries. Computation of spectra for the interpretation of experimental data is already commonplace in the chemistry community and slowly permeating investigations of chemical-mechanical investigations.

**Major advances are expected and required.** Accessing realistic time-scales is still very much an issue. While time-acceleration techniques exist, these are limited to particular systems and make simplifications that make them difficult to apply to system with structural heterogeneity, such as glasses (where they are most important because of slow relaxation or ageing processes and logarithmic strain-rate dependencies of driven processes). Furthermore, usefully accurate descriptions (with controlled uncertainty) of multicomponent systems that scale  $O(N)$  are still lacking, in particular for oxides and interactions with the environment (e.g.,  $O_2$  and  $H_2O$ ). Expensive DFT calculations can capture chemical complexity but are typically too slow to be combined with phase-space sampling techniques. Our current capability for modelling the microstructural level material response is limited. Addressing this requires making connections to mesoscale theories such as non-equilibrium statistical mechanics.

More generally, advances are inhibited by the limited knowledge that each community has of the techniques used by other communities. Cross-fertilisation of ideas from different experimental and simulation techniques should be accelerated (through workshops and bilateral exchanges/visits) and more research projects should try to combine different simulation techniques to scale up results of small-scale techniques or validate the results of large scale methods.

**Obstacles to success.** The participants expressed concern that real systems are so complex that it is hard to disentangle individual processes in experiments, suggesting that simpler experiments on model materials should be carried out where possible. Examples include experiments on steels, which are difficult to capture with atomistic techniques because of their chemical complexity. Experiments should, for example, start by looking at highly pure iron sample (which is not technologically relevant) and then introduce alloying elements in a controlled manner.

Another concern in the emerging area of big data was the proper acknowledgment of data uploaded by a third-person and then used in research by another party, as well as indicators for the precision of simulation data. Data stored in databases should be reproducible. These questions all boil down to mutual trust with data quality and handling of data.

**Infrastructure requirements.** A specific concern voiced was the development and long-term maintenance of codes. It was suggested that CECAM could play a role here in aiding development of software. Software specialists that increase the efficiency of codes would also be helpful. A concern voiced was ensuring a sustainable career structure for software specialists both inside and outside academia. Databases should be created to publicly save and share experimental and simulation data. It was particularly noted that providing modellers with access to direct numerical results from experiments has the potential for significant impact.

**Funding council requirements.** The long-term maintenance of codes requires significant funds that are not currently provided by the major funding councils. Academic institutions and funding agencies should enforce the formation of working groups composed by both theorists and experimentalists as well as a focus on mechanisms and not on specific techniques. This would encourage collaboration between experimentalists and theorists. In this context theorists should be encouraged to propose and design experiments, and experimentalist should propose and design simulations.

**Addressing the needs of industry to drive economic growth.** Industrial workshop attendees from ExxonMobil, BP and BMW informed a discussion of how to enhance academic engagement with industry, e.g. through network forming opportunities. It's important that these should also include PhD students to aid them in searching for jobs. There should generally be clarity on the expectations from both sides and academia should make realistic promises of what can be achieved within the timescale of a PhD or postdoc project. Challenging industrial problems should inspire methodological development rather than being viewed as special cases of previous academic work.

Another mechanism to facilitate collaboration between academia and industry should be opportunities for co-funding of small projects. The French system was cited as having a useful program where single PhD positions could be co-funded 50% by industry and the government. EU Horizon 2020 or German BMBF projects were considered too large to be useful for efficient targeted research. Industry sabbaticals were cited as opportunities for more senior scientists. However, the workshop participants expressed some concern that over-concentration of resources on industrial R&D problems could ultimately be self defeating, since people trained to solve problems actually constitute a major output of blue sky academic research. Explaining to funders and stakeholders when ideas have arisen which were unexpected at the start of projects may help.

**Recommendations to CECAM and Psi-k.** The participants identified key roles that CECAM and Psi-k could play:

- facilitate two-way exchanges/internships/sabbaticals between academia and industry, e.g. by maintaining lists of industrial contacts
- hosting introductory materials modelling courses for *experimental* PhD students
- establish challenge problems in canonical systems common to experimentalists and modellers
- maintain a database of funding sources for researcher exchange and programs for academia/industry exchange
- encourage workshop organisers to foster cross-fertilisation of different fields both in terms of experiment/theory and in terms of different techniques
- support the sustainable development of software codes through hosting of coding efforts
- finally, there was considerable enthusiasm for the establishment of a CECAM node in the USA.

# 1 Description

The response of many materials to external loads is not directly determined by their bulk mechanical properties, but is instead mediated by chemical and structural transformations, often nucleating at defects or interfaces, and involving reactions with environmental chemical species. As a result, a specimen's macroscopic mechanical response will in fact depend on the properties of the transformed material, the structure of which is typically unknown and very often difficult to characterize. However, the members of the scientific community interested in modelling mechanical properties are often not experts in modelling the materials' bulk and surface chemistry, and its coupling with externally imposed compression and tension.

This workshop aims to bring together experts from all the relevant modelling fields to discuss materials science and engineering aspects of tribology, fracture mechanics, and plasticity that involve chemical and structural modifications induced by mechanical loading. Our underlying assumption is that multiscale modelling of processes originating within the "process zone" of (point-like) asperity contacts, (1D) crack tips, or (2D) alloy interfaces is necessary to fully understand wear, stress corrosion, and creep/plasticity, and could suggest new engineering approaches for their control.

There are many examples of this. In specimens subject to tribological load, the material right beneath the sliding surfaces often undergoes microstructural transformations [1,2]. The extreme pressures reached at asperity-asperity contacts can also lead to intermixing of chemical elements from the contacting bodies [3], which may cause the formation of tribomaterials with entirely different stoichiometry and properties. Tribological loads may furthermore induce reactions with air or lubricant molecules, leading to surface terminations [4], or hundred-nanometer-thick glassy films [5] whose formation chemistry is not yet understood.

In fracture, gas- and liquid-phase molecules interact with crack tips, inducing bond breaking [6] or even diffusing into the near tip region, thus drastically modifying the material's fracture toughness. Stress-corrosion cracking in silica glass is e.g., thought to involve coupled nucleation of voids, rearrangement of the amorphous structure and diffusion of water ahead of a crack tip [7].

Finally, plastic deformation can also involve transformations that strongly affect the material's properties. For instance, glasses deform (and fail) in shear bands that carry a clear structural signature of deformation [8] such as changes in density. Moreover, large-scale migration of the interfaces between  $\alpha$ - $\beta$ -phases in Ni superalloys occur in response to temperature [9] and mechanical load cycles [10] as a result of the coupling between local chemistry (via point-defect diffusion) and long-range stress.

Modelling the structural and chemical modifications of the "base" material in realistic operating conditions is essential for all the processes above. However, doing this accurately is at the very limit of what is currently achievable, and invariably requires a multidisciplinary approach, and contributions/expertise from different but neighbouring fields, such as surface chemistry, high-pressure physics and amorphous solid mechanics.

## Goals

The workshop will focus on the three subfields identified above: tribochemistry and related microstructural changes, crack-tip chemistry, and plasticity in glassy and metallic materials. An improved understanding of all these processes is needed and has the potential for significant technological and, down the line, societal/economic impact.

Special focus will be given to identifying the most relevant open problems, particularly those which can be attacked by combining existing techniques from the three subfields. Ample time will be allocated to discussing how to combine the different available modelling techniques, and integrate them with high-precision experimental techniques. This is expected to naturally lead to new links/collaborations. The specific case studies up for discussion are listed below.

### (1) Chemistry at sliding surfaces.

Surface chemistry [4] and atom-by-atom processes under realistic tribological conditions. Making progress here will require coupling chemical accuracy to long-range stress fields.

Subsurface material damage under severe load. This typically includes grain structure changes in crystalline materials [1] and local short-range order in glasses.

Slow processes such as frictional ageing [11] or grain refinement under small-amplitude, low-frequency load, requiring time-acceleration techniques and/or mesoscale models.

### (2) Chemistry of fracture.

Stress corrosion cracking under the influence of hydrogen, oxygen or water: this requires methods to couple the long-ranged atomistic field to the quantum chemistry at the crack tip (so far limited to crystalline covalent materials [6,12]).

Crack growth in amorphous materials. This requires faithful force-fields for network glasses that describe both small-scale ductility and large-scale brittleness.

Combined action of structural transformations and diffusion of ambient species (e.g. water) at crack tips during stress corrosion cracking, also directly relevant for hydromechanical rock-fracturing (“fracking”). This combines the previous two points.

### (3) Plasticity in glassy and metallic materials.

Plastic deformation of glasses. A description of shear banding requires faithful force-fields and the identification of order parameters describing the local structural character of shear bands, to distinguish them from the surrounding bulk [8].

Plastic deformation in complex alloys. The plasticity response in Ni-based superalloys is strongly coupled to dynamically transforming matrix/precipitate interfaces [10].

The interaction with a chemically complex external environment is common to all three topics: this is self-evident in stress corrosion cracking, but also very important for tribochemical processes and deformation of glasses. Moreover, feedback from (3) to (1) and (2) is inevitable due to the plastic deformations that occur during, and influence the evolution of, fracture and tribological processes.

Accurately modelling these “chemomechanical” processes is very challenging, as it typically requires coupling QM-based local chemical descriptions with large model systems to capture stress relaxation, which in realistic (e.g., three-dimensional, amorphous) systems requires petascale computational resources and non-uniform precision (e.g., QM/MM) techniques.

The three topics are also connected by the simulation techniques used to study them, each with specific strengths and limitations. The workshop will specifically explore how the classical interatomic potentials - or density functional theory-based methods - used to model tribology and plasticity could benefit the study of fracture, and by converse how the techniques combining these already used in fracture-modelling could be fed back to plasticity and tribology studies.

There is, in particular, considerable scope for exchanging ideas to address questions such as:

How can the system size restrictions of current high-precision modelling be reconciled with the size- and time-complexity of the problems at hand, and can big-data and/or machine learning approaches help?

How can we optimise the information flow between the different time- and length scales involved - particularly, when is hierarchical (parameter passing) multiscale modelling sufficient, or when is coupled (e.g., QM/MM) multiscale modelling instead necessary?

Where should our method development effort focus in the next 2-3 years? Classes of options include:

Improving hybrid embedding techniques, make them e.g., more user friendly, easier to validate, and more modular/inter-operable

Coarse graining of atomistic simulations to construct mesoscale models

Rare events and free energy exploration schemes - possibly importing knowledge from the biochemical community to study slow processes and extrapolate to long time scales

What is the best use of existing methods to avoid duplication/wasted effort? e.g. parameterising new classical potentials for each new problem.

Travel Support for US-based researchers

U.S.-based participants can apply for travel funding through the [travel award](http://mcc.illinois.edu/travel/) program of the Materials Computation Center of the University of Illinois at Urbana-Champaign (NB: this scheme does not support invited speakers).

### Key references

- [1] Romero et al., *Phys. Rev. Lett.* 113, 036101 (2014)
- [2] Pastewka et al. *Nature Mater.* 10, 34 (2011)
- [3] Rigney, Karthikeyan, *Tribol. Lett.* 39, 3 (2010)
- [4] Konicek et al., *Phys. Rev. B* 85, 155448 (2012)
- [5] Martin et al., *Tribol. Lett.* 50, 95 (2013)
- [6] Gleizer et al., *Phys. Rev. Lett.* 112, 115501 (2014)
- [7] Pallares et al., *J. Am. Ceram. Soc.* 94, 2613 (2011)
- [8] Falk, Langer, *Annu. Rev. Condes. Matter Phys.* 2, 253 (2011)
- [9] Woodward et al., *Acta Mater.* 75, 60 (2014)
- [10] Haghghat et al., *Acta Mater.* 61, 3709 (2013)
- [11] Liu, Szlufarska, *Phys. Rev. Lett.* 109, 186102 (2012)
- [12] Moras et al., *Phys. Rev. Lett.* 105 075502 (2010)

## 2 Program

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### Day 1 - Tuesday September 1, 2015

#### Registration and welcome

- 13:00 to 14:00 - Registration
- 14:00 to 14:20 - Welcome and Introduction

#### Afternoon session

- 14:20 to 15:00 - **Peter Gordon**  
Making a case for multiscale – an industrial perspective from the energy industry
- 15:00 to 15:40 - **Christopher Woodward**  
Ni-based superalloy casting parameters from ab-initio molecular dynamic simulations
- 15:40 to 16:00 - Coffee Break
- 16:00 to 16:40 - **Erik Bitzek**  
Atomistic simulations of dislocation-interface interactions in the microstructure of ni-base superalloys
- 16:40 to 17:20 - **Michael Moody**  
Atom probe tomography characterisation to correlate nanostructure to materials in-service performance
- 17:30 to 18:30 - Poster Session

### Day 2 - Wednesday September 2, 2015

#### Morning session

- 9:00 to 9:40 - **Jutta Rogal**  
Capturing the kinetics of complex phase boundary migration: an adaptive kinetic monte carlo study
- 9:40 to 10:20 - **Gabor Csanyi**  
Calculating phase diagrams of materials with nested sampling
- 10:20 to 10:50 - Coffee Break
- 10:50 to 11:30 - **Noam Bernstein**  
Free energy calculation methods and applications to solids
- 11:30 to 12:10 - **Mikko Alava**  
Cracks and time-dependent transformations
- 12:10 to 14:00 - Lunch

### Afternoon session

- 14:00 to 14:40 - **Dov Sherman**  
Complex dynamic stress corrosion cracking in silicon crystal
- 14:40 to 15:20 - **Derek Warner**  
Illuminating the chemo-mechanics of hydrogen enhanced fatigue crack growth in aluminum alloys
- 15:20 to 15:50 - Coffee Break
- 15:50 to 16:30 - **Cindy Rountree**  
Effect of composition on stress corrosion fracture and fracture toughness in pristine and irradiated glasses
- 16:30 to 17:10 - **Matteo Ciccotti**  
Micromechanisms of fracture propagation in glassy polymers
- 17:30 to 20:30 - Poster Session with cold buffet sandwiches

### Day 3 - Thursday September 3, 2015

#### Morning session

- 9:00 to 9:40 - **Sidney Yip**  
Atomistics of creep in metallic glasses: shear transformations and instability at slow strain rates
- 9:40 to 10:20 - **Anne Tanguy**  
Compositional effects on the constitutive mechanical laws in silicate glasses
- 10:20 to 10:50 - Coffee Break
- 10:50 to 11:30 - **Svenja Bachmann**  
Friction reduction in bmw-powertrain application - a contribution to achieving co2 objectives
- 11:30 to 12:10 - **Michael Moseler**  
Atomic scale understanding of plowing friction and wear on simple metal surfaces
- 12:10 to 14:00 - Lunch

#### Afternoon session

- 14:00 to 14:40 - **Michael FALK**  
A multi-bond model of single-asperity wear at the nano-scale
- 14:40 to 15:20 - **Filippo Mangolini**  
Fundamental surface-analytical investigations of shear-induced mechanochemistry

- 15:20 to 15:50 - Coffee Break

#### **Breakout session followed by plenary session**

- 15:50 to 16:40 - Round Table Discussion: Future Directions
- 16:40 to 17:30 - Discussion-Conclusions
- 19:30 to 22:00 - Social Dinner

#### **Day 4 - Friday September 4, 2015**

##### **Morning session**

- 9:00 to 9:40 - **Izabela Szlufarska**  
Tribological properties of cu alloys by atomistic simulations
- 9:40 to 10:20 - **Michael Chandross**  
A general, predictive model of friction in metallic contacts
- 10:20 to 10:50 - Coffee Break
- 10:50 to 11:30 - **William Curtin**  
Mechano-chemistry of fracture and plasticity
- 11:30 to 12:00 - Closing Word

## 3 Abstracts

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### ***Making a case for multiscale – an industrial perspective from the energy industry***

Peter Gordon[1]

ExxonMobil Research & Engineering

The interplay between mechanics, chemistry, and material evolution under conditions of service can be of critical importance in determining the efficacy of industrial operations in the energy industry, as related to seemingly disparate issues of equipment durability, catalyst performance, product quality, and reservoir fracture performance, to name a few. In this talk, we will highlight several examples where an understanding of mechanical-chemical coupling is essential in determining the overall performance of a system, drawing on examples that cut across the major sectors of our business. In some cases, modeling can be performed at an acceptable level of resolution with existing and emerging tools, and we will discuss ongoing efforts within our lab aimed at tackling these problems. In others cases, the gap between what is possible and what is needed remains large, and we will attempt to articulate what we believe is necessary to enable modeling approaches to progress to a point where they can become part of the industrial modeler's toolbox.

### ***Ni-based superalloy casting parameters from ab-initio molecular dynamic simulations***

Christopher Woodward[1], J. Lill

Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH 45433

2High Performance Computing Modernization Program / User Productivity Enhancement, Technology Transfer and Training, WPAFB, OH 45433

Optimization and control of casting process-parameters can significantly improve the properties, including life, of directionally solidified turbine airfoils. The casting process window is often limited by alloy chemistry, component geometry and possible formation of casting defects. An ab-initio molecular dynamics approach is used to predict fundamental parameters of molten Ni-based superalloys with the goal of informing models of defect formation during solidification process. The Density Functional Theory calculations are applied to molten Ni-based superalloys ranging from model alloys to Rene-N4, Rene-N5 and CMSX-4 in order to predict density, shear viscosity, diffusion rates and local ordering. Calculated densities are consistent with densities interpolated from binary alloy measurements and limited measurements of commercial alloys. Density inversion is also predicted for some of the molten alloys for compositions and temperatures expected in the mushy zone. A new dimensionless parameter is proposed for the temperature dependent materials properties that control defect formation during casting.

### ***Atomistic simulations of dislocation-interface interactions in the $\gamma/\gamma'$ microstructure of ni-base superalloys***

Erik Bitzek[1], Frederic Houllé, Juan Wang, Julien Guénoilé, Johannes J. Möller, Aruna Prakash

Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Department of Materials Science and Engineering, Institute I, Erlangen, Germany

The superior strength of single crystalline Ni-base superalloys is mainly caused by the high volume fraction of the cuboidal L12 ordered  $\gamma'$  hardening phase which is precipitated in a disordered face-centered cubic  $\gamma$  matrix. The strengthening effect is rooted in the difficulty of channel dislocations in the  $\gamma$ -phase to cut into the  $\gamma'$ -precipitate. The interaction of dislocations with the  $\gamma/\gamma'$  interphase boundary (IPB) is an inherently atomistic problem related to the dislocation core structure and energy within the

different phases as well as to the interface structure and the local chemical composition. In this talk we present recent results on two complementary simulation setups. The critical resolved shear stress  $\bar{\tau}_c$  required for dislocations in the  $\hat{\Gamma}^{\beta}$  matrix to penetrate into the  $\hat{\Gamma}^{\alpha}$ -phase was determined by applying force boundary conditions on infinitely long, straight dislocation lines interacting with a coherent planar (100) IPB in a quasi-2D simulation setup. This setup allows one to incorporate screw dislocations as well as  $60^\circ$  mixed dislocations. The atomic interaction is modeled by two different embedded atom method (EAM) type potentials. Studying different types of dislocations and using different potentials allows one to evaluate the influence of lattice misfit on the critical cutting stress, and to correlate  $\bar{\tau}_c$  with potential properties like the stable and unstable stacking fault energies. In addition to the determination of  $\bar{\tau}_c$  in a pure Ni/Ni<sub>3</sub>Al system, the influence of Al concentration gradients across the coherent IPB on  $\bar{\tau}_c$  was investigated. These results can be directly used to parameterize e.g. dislocation dynamics (DD) simulations. Further simulations were performed on fully 3D systems. A novel technique was developed to reconstruct an atomistic sample from an APT experiment on the alloy ERBO/1 [1]. The curvature of the reconstructed precipitate leads to the formation of a misfit dislocation network (MFDN), which is significantly different from the MFDN obtained for a planar interface. Unlike the constricted misfit dislocation cores obtained in the usual 2D setups, the misfit dislocations can dissociate, and the overall network structure is reminiscent of the interfacial dislocation network formed during the initial stages of creep, and contains the same Burgers vectors and line directions. Simulations of the interaction of one and two  $60^\circ$  channel dislocations with the MFDN reveal typical processes also observed in experiments like the knitting out of dislocations from the MFDN and the cutting of the precipitate by a pair of channel dislocations. These results cannot be obtained with simulation setups that were previously used in the literature [2]. As APT does not only provide information on the sample morphology but also on its chemical composition, the simulations were performed using stoichiometric Ni/Ni<sub>3</sub>Al as well as with representative local concentrations of Ni, Al and Re, thus allowing to assess the role of chemical composition on the dislocation – precipitate interactions.

[1] A. B. Parsa et al., *Advanced Scale Bridging Microstructure Analysis of Single Crystal Ni-Base Superalloys*. *Advanced Engineering Materials* 17, 216-230 (2015).

[2] A. Prakash et al., *Atom probe informed simulations of dislocation – precipitate interactions reveal the importance of local interface curvature*.

*Acta Materialia* 92, 33-45 (2015).

### **Atom probe tomography characterisation to correlate nanostructure to materials in-service performance**

Michael Moody[1], Paul Bagot

Department of Materials, University of Oxford

Atom probe tomography (APT) is a 3D atomic scale microscopy technique. Its combination of very high spatial and chemical resolution provides unique insights that are highly complementary to other characterisation techniques and modelling. Hence, APT is playing an increasingly prevalent role in the design of new materials, correlating microstructure to performance and research into certain failure mechanisms in structural materials. This talk will provide a brief introduction to APT and present three examples of research underpinned by this technique: the effect of boron on grain boundary character in a new polycrystalline superalloy; solute redistribution within a white etching area formed by rolling contact fatigue in a bearing steel[1]; characterisation of a stress corrosion crack tip in a PWR stainless steel[2].

[1] J. H. Kang et al., *Scripta Materialia* 69, 630 (2013).

[2] M. Meisnar et al., *Micron* (2014).

### **Capturing the kinetics of complex phase boundary migration: an adaptive kinetic monte carlo study**

Jutta Rogal[1]

Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr University Bochum

Atomistic modelling of the dynamics of phase transformations is a particularly challenging task. If the mechanism of the phase transformation is governed by so-called rare events then the time scale of interest will reach far beyond the capabilities of regular molecular dynamics simulations. The atomistic rearrangements during solid-solid phase transformations in bulk systems involve massive structural changes including concerted multi-atom processes. The interface between two structurally different phases leads to a complex energy landscape that needs to be explored during the dynamical evolution of the interface. Here, we employ an adaptive kinetic Monte Carlo (AKMC) approach to investigate such processes at the interface between cubic and topologically close-packed phases in transition metals. In particular we investigate the transformation between BCC and A15 in molybdenum. During the dynamical simulations a finite, disordered interface region evolves to compensate the structural mismatch between the two crystal phases. This disordered interface region makes the identification of a single transformation mechanism difficult. Still, from our simulations we extract a rate for the layer transformation which we relate to an effective barrier for the transformation mechanism and discuss the corresponding features of the complex energy landscape along the transformation path.

### ***Calculating phase diagrams of materials with nested sampling***

Gabor Csanyi[1], Rob Baldock, Livia B. Partay, Albert P. Bartok, Mike Payne  
Engineering Laboratory, University of Cambridge

We extend the Nested Sampling algorithm to simulate materials under periodic boundary and constant pressure conditions, and show how it can be efficiently used to determine the phase diagram directly from the potential energy in a highly automated fashion. The only inputs required are the composition and the desired pressure and temperature ranges, in particular solid-solid phase transitions are recovered without any a priori knowledge about the structure of solid phases. We apply the algorithm to the Lennard-Jones system, aluminium, and the NiTi shape memory alloy.

### ***Free energy calculation methods and applications to solids***

Noam Bernstein[1]

Naval Research Laboratory, Washington DC

The free energy surface (FES) describes the equilibrium behavior of a system in terms of a limited number of collective coordinates in the presence of disorder and fluctuations due to temperature. The FES can be computed as the logarithm of the probability distribution of the system, or its gradient can be directly sampled, in a canonical (constant temperature) simulation. In either approach the computational expense inevitably leads to substantial noise in the measurements. We show how Gaussian process regression (GPR), a Bayesian multidimensional interpolation technique that is robust in the presence of noise, can be used to accurately extract the smooth FES from noisy measurements. We discuss two aspects of the task of computing the FES of an atomistic system. The first and simpler of the two is the reconstruction of the entire FES of polyaniline molecules from samples on a regular grid in collective coordinate space of 1, 2, and 4 dimensions. We compare our GPR-based reconstruction to two state-of-the-art multidimensional FES calculation methods, least-squares radial basis function reconstruction (LSRBF) and the variational free energy profile method (vFEP). The second aspect is exploration: where and how to best move around the multidimensional space to find the relevant (i.e. relatively low free energy) region. We compare the computational efficiency of various combinations of exploration and reconstruction algorithms and check the accuracy of using data gathered during exploration for

reconstruction. Finally we present an application of free energy calculation methods to temperature and composition driven structural transformations in LiBH<sub>4</sub>, a proposed solid electrolyte Li-ion conductor.

### ***Cracks and time-dependent transformations***

Mikko Alava[1]

Aalto University, Department of Applied Physics

The coarse-grained statistical mechanics of cracks is now fairly well established: there is a range of coarse-grained models, and there are clear indications of signs of open problems where these models do not match reality - as well as of cases where theory predictions fit with experiments. In this talk I will review both these issues, and then consider several directions in which microscopic "time-dependent" information should be coupled to such models.

### ***Complex dynamic stress corrosion cracking in silicon crystal***

Dov Sherman[1], Anna Gleizer

Dept. of Materials Science and Engineering, Technion, Haifa-32000, Israel

It was reported recently that the cleavage energies at initiation for the (110)[1-10] and (111)[11-2] low energy cleavage systems of silicon at room conditions are  $2.7 \pm 0.3$  and  $2.2 \pm 0.2$  J/m<sup>2</sup>, respectively. These energies are  $3.5 \pm 0.2$  and  $2.9 \pm 0.2$  J/m<sup>2</sup>, respectively, under 99.996% Ar at atmospheric pressure. It was demonstrated by atomistic simulations that O<sub>2</sub> molecules play the role of a corrosive agent capable of initiating cracks on the low energy cleavage systems of silicon crystal at subcritical loads. These results, obtained for relatively slow cracks at initiation, are indicating on stress corrosion cracking mechanisms (Gleizer et al., Phys. Rev. Lett. 112, 115501, 2014). The latter results are with excellent agreement with DFT calculations of twice the surface energy,  $2\gamma$ , of 3.46 J/m<sup>2</sup> and 2.88. Recent cleavage fracture experiments revealed two unexpected and distinct dynamic stress corrosion cracking mechanisms when crack was propagated on the above low energy cleavage systems of silicon crystal under pure mode I. The experiments were performed in air. While the first cleavage system showed velocity dependent stress corrosion cracking mechanism, initiating at energy of 2.7 J/m<sup>2</sup> and terminating at 3.5 J/m<sup>2</sup> at speed of 1,250 m/sec, that on the latter is clearly velocity independent at 2.2 J/m<sup>2</sup> up to a measured crack speed of 1,200 m/sec. The dynamic stress corrosion cracking energies were evaluated using Freund equation of motion. Apparently, the distinct behavior is due to the distinct atomistic arrangement at the crack tip of both low energy cleavage planes.

### ***Illuminating the chemo-mechanics of hydrogen enhanced fatigue crack growth in aluminum alloys***

Derek Warner[1], Richard Zamora, Kristopher Baker

School of Civil and Environmental Engineering, Cornell University

Abstract: The presence of elemental hydrogen is known to accelerate fatigue crack growth in aluminum alloys. However, a direct link between experimental data and a governing atomistic mechanism has remained elusive. Here we present a series of computational studies, across multiple length scales, directly linking an atomistic mechanism to experimental data for a specific aluminum alloy. Starting with an ab initio investigation of hydrogen bonding near a {111} aluminum surface, we quantify the effects of hydrogen surface impurities on slip and decohesion, finding evidence of general bond weakening in the presence of atomized hydrogen surface impurities. We then modify an aluminum-only interatomic potential to reproduce ab initio trends by strategically shielding critical surface bonds in accordance with

the environmental exposure level. The strategic shielding model is used within a coupled atomistic-continuum discrete dislocation framework to predict the effect of hydrogen on near threshold fatigue crack growth rates. The predicted trends agree with published experimental data, suggesting that Hydrogen Enhanced Decohesion (HEDE) and Adsorption Induced Dislocation Emission (AIDE) play a joint role in the failure of aluminum alloys in humid environment.

### ***Effect of composition on stress corrosion fracture and fracture toughness in pristine and irradiated glasses***

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From the windshields in our cars to the glass dishes which we cook with to the storage of nuclear waste, oxide glasses have widespread use. The extensive use of oxide glasses can be attributed to amorphous structure, optical transparency, electrical and heat insulation, and large hardness. However, oxide glasses have a major drawback: brittleness. Even small flaws in the structure can lead to the ultimate failure of the material. Oxide glasses' brittleness can be partly attributed to the homogeneities at large length scales. However, failure properties are driven by the heterogeneities at small length scales, i.e. the nanoscale. Understanding how minute structural variations dictate the continuum level failure of materials is intrinsically important in assessing the life-time of materials. Herein, minute structural variations occur via "tweaking" the glass structure (i.e. varying the chemical composition of glasses and/or the structure via irradiation of glasses). Studies herein concern 7 SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O (SBN) Ternary glass systems. "Tweaking" the ratios of SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O gives way to alterations in the structural and mechanical properties of the glasses and subsequently variations in the fracture process. To better understand how these chemical compositions relate structural variations to continuum level properties, the sample are irradiated with electrons. The suite of experiments exposes macro to micro fracture variations. Initially, the hardness tests of the glasses aid in understanding the plastic deformation as determined via indentation tests. The presentation will focus on stress corrosion fracture damage and how it varies with chemical composition and irradiation.

### ***Micromechanisms of fracture propagation in glassy polymers***

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While most glassy polymers are nominally brittle at macroscopic scales, they are known to exhibit plastic deformation in indentation, scratching, and microcutting when the loaded region is sufficiently small. The same applies to the micrometer size process zone at the tip of a propagating crack. While the presence and approximate size of this microscale plastic zone is well described by the Dugdale model, the prediction of the toughness of these materials is not possible without accounting for the details of the local large strain field and the work hardening behaviour of these polymers, which can be inferred from their response to compressive tests. Strain localization mechanisms such as crazing or shear banding should also be taken into account to properly model toughness. Finally, viscoplastic creep plays a major role in determining the dependence of the toughness on crack propagation velocity, as well as the important difference between the initiation and propagation toughness, which is responsible for the occurrence of a characteristic stick-slip propagation under some loading conditions. We present here the important insights that can be obtained from an in-situ experimental investigation of the strain fields

in the micrometric neighbourhood of a propagating crack. Atomic Force Microscopy combined with Digital Image Correlation reveals to be a very rich technique for our aim, although it limits our observations to the external surface of the sample and to very slow crack propagation (below nm/s). As an example, Figure 1 reports the very different look of fractures propagating at similar slow velocities in PMMA and epoxy resin. The consequences of these observations on understanding the toughness of glassy polymers will be discussed, as well as their implication on the fracture behaviour of these polymers in very confined conditions such as when used as a matrix of a long fiber composite material. This work was supported by the ANR project PROMORPH (ANR-11-RMNP-0006)

### ***Atomistics of creep in metallic glasses: shear transformations and instability at slow strain rates***

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Time-dependent phenomena such as stress relaxation avalanches [1] and shear band formation [2] are of current interest in understanding amorphous plasticity and the effects of strain rate. We study tensile strain evolution in a model metallic glass by atomistic simulation in which transition-state pathways across an energy landscape with multiple minima and saddle points are sampled using a meta-dynamics algorithm [3]. Three stages of creep behavior, transient (logarithmic in time), steady-state (linear), and tertiary (diverging) are observed at strain rates comparable to experiments. The corresponding atomic configurations at each stage reveal the role of local shear transformations, from independent nucleation events during the early stage to concerted shear band formation and growth in the later stage. Implications of the simulation findings as complementary results to theoretical and experimental studies will be discussed.

[1] J. Antonaglia et al., *Phys. Rev. Lett.* 112, 155501 (2014).

[2] J-O. Krispneit et al., *Nature Communications* 5:3616 (2014).

[3] P. Cao et al., *Phys. Rev. E* 86, 016710 (2012).

### ***Compositional effects on the constitutive mechanical laws in silicate glasses***

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Institut Lumière Matière, Lyon

Silicate glasses are examples of structural glasses with network modifiers. As any disordered material, they can age and deform inhomogeneously. We studied the response to external mechanical load at very low temperature with the help of atomistic simulations. We showed that the strain resolution is crucial to measure the elastic properties of disordered materials. Moreover, combining shear and compressive mechanical deformation, we were able to reconstruct hardening yield surfaces in stress space, parametrized by the residual shear strain and densification, and compared it with the nucleation of local plastic rearrangements. In the case of silicate glasses, we showed that sodium plays a very specific role in heterogeneous elasticity, and acts as a seed for the plastic deformation.

### ***Friction reduction in bmw-powertrain application - a contribution to achieving co2 objectives***

Svenja Bachmann[1]

BMW Group

The European automobile industry has entered into a commitment to drastically reduce mean fleet CO<sub>2</sub> emissions. In this context BMW has started several new projects and some of these topics will be discussed in the presentation. The application of DLC coatings represents one approach to reduce friction and wear in tribological applications. However, it is not fully understood how low friction coefficients can be achieved reliably using amorphous carbon coatings. In order to improve the basic understanding of the friction and wear behaviour of lubricated DLC coatings, tribological experiments were conducted and subsequently analysed using various techniques. Some of these tribological experiments and analytical results will be presented. The aim is to develop systems with low friction coefficients suitable for use in powertrain applications.

### ***Atomic scale understanding of plowing friction and wear on simple metal surfaces***

Michael Moseler[1]

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Wear and removal of material from metal surfaces is inherently connected to plastic flow. In this talk I present investigations of plowing-induced unconstrained surface plastic flow on a nanocrystalline copper surface [1] as well as on graphene covered Pt surfaces [2]. Both systems have been studied by massive molecular dynamics simulations and atomic force microscopy scratch experiments. In agreement with experimental findings, bulges on the nanocrystalline Cu surface in front of a model asperity develop into vortex-like fold patterns that mark the disruption of laminar flow. We identify dislocation mediated plastic flow in grains with suitably oriented slip systems as the fundamental mechanism of bulging and fold formation. The observed folding can be fundamentally explained by the inhomogeneity of plasticity on polycrystalline surfaces which favors bulge formation on grains with suitably oriented slip system. This process is clearly distinct from Kelvin-Helmholtz instabilities in fluids, which have been previously suggested to resemble the formed surface fold patterns. The generated prow shows distinct grain coarsening [3] and grows into a rough chip with stratified lamellae that are identified as the precursors of wear debris. Our findings demonstrate the importance of surface texture and grain structure engineering to achieve ultralow wear in metals. The wear behavior of graphene-covered Pt(111) surfaces has been inferred using nanoindentation and nanoscratching. We find elastic response of the system at low load, plastic deformation of Pt below the graphene at intermediate load, and eventual rupture of the graphene at high load. Friction remains low in the first two regimes, but jumps to values also found for bare Pt(111) surfaces upon graphene rupture. While graphene substantially enhances the load carrying capacity of the Pt substrate, the substrate's intrinsic hardness and friction are recovered upon graphene rupture. The results indicate that coating metals with graphene can increase their plowing resistance resulting in wear reduction provided the applied load are small enough to prevent the graphene from rupturing.

[1] Nils Beckmann, Pedro A. Romero, D.Linsler, Martin Dienwiebel, Ulrich Stolz, Michael Moseler, Peter Gumbsch, *Origin of folding instabilities on polycrystalline metal surfaces*, *Phys. Rev. Applied* 2, 064004 (2014)

[2] Andreas Klemen, Lars Pastewka, Soorali Ganeshamurthy Balakrishna, Arnaud Caron, Roland Bennewitz, Michael Moseler, *Atomic Scale Mechanisms of Friction Reduction and Wear Protection by Graphene*, *Nano Letters* 14, 7145 (2014)

[3] Pedro A. Romero, Tommi T. Järvi, Nils Beckmann, Matous Mrovec, and Michael Moseler, *Coarse graining and localized plasticity between sliding nanocrystalline metals*, *Phys. Rev. Lett.* 113, 036101 (2014)

### ***A multi-bond model of single-asperity wear at the nano-scale***

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Johns Hopkins University

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Single-asperity wear experiments and simulations have identified different regimes of wear including Eyring- and Archard- like behaviors. A multi-bond dynamics model based on Filippov et al. [1] captures both qualitatively distinct regimes of single-asperity wear under a unified theoretical framework. In this

model, the interfacial bond formation, wearless rupture and transfer of atoms are governed by three competing thermally activated processes. The Eyring regime holds under the conditions of low load and low adhesive forces; few bonds form between the asperity and the surface and wear is a rare and rate-dependent event. As the normal stress increases the Eyring-like behavior of wear rate breaks down. A nearly rate-independent regime holds under high load or high adhesive forces; bonds form readily and the resulting wear is limited by the sliding distance. In restricted regimes of normal load and sliding velocity, the dependence of wear rate on normal load is nearly linear, as described by the Archard equation. Detailed comparisons to two experimental investigations and one set of molecular dynamics simulation data illustrate both regimes and the cross-over between the two described by this unifying theory.

[1] *Phys. Rev. Lett.* 92, 135503 (2004)

### ***Fundamental surface-analytical investigations of shear-induced mechanochemistry***

Filippo Mangolini[1], K.D. Koshigan [1], N.N. Gosvami [2], J.B. McClimon [3], J.A. Bares [2], D.G. Yablon [4], J. Fontaine [1], R.W. Carpick [2]

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Tribology is the study of interacting surfaces in relative motion and the resulting phenomena of friction, lubrication, and wear. Energy and material losses in moving mechanical components as a result of friction and wear impose an enormous cost on national economies and call for the development of improved engineering systems with reduced friction and wear. Establishing a fundamental understanding of the phenomena occurring at sliding interfaces and controlling the observed tribological performance constitutes a critical step in the rational design and synthesis of new, modified, and improved materials and lubricants that can reduce energy and resource consumption in tribological applications. The development of this understanding is a challenging materials science problem due to the complex nanoscale phenomena occurring at buried sliding interfaces, where chemical transformations are strongly affected by the resultant stresses. A key step in tackling this challenge lies in applying advanced surface-analytical methods to the study of tribological materials and interfaces. In this talk, I will present recent experimental results focusing on fundamental surface-analytical investigations of: a) the structural changes occurring on solid lubricants upon sliding under different environmental conditions; and b) the formation and growth of tribofilms formed by antiwear additives used in automotive engine lubricants, gear oils, and greases. First, I will discuss the mechanochemical transformations that occur in high performance solid lubricant thin films during tribological sliding. By using an advanced synchrotron-based imaging method based on near edge X-ray absorption fine structure (NEXAFS) spectroscopy, we gained insights into the transformations occurring in silicon oxide-doped hydrogenated amorphous carbon (a-C:H:Si:O) surfaces upon sliding under different environmental conditions [1]. a-C:H:Si:O is a promising class of amorphous carbon materials for several applications (hard-disk drives, satellites) since it exhibits enhanced thermal stability as well as good tribological performance across a broader range of environments compared to hydrogenated amorphous carbon (a-C:H). Yet, the scientific basis for this promising behaviour of a-C:H:Si:O is not fully understood. By analysing the mechanochemical transformations occurring in a-C:H:Si:O as a function of the sliding environment, we highlighted the

major role of the environment in affecting the tribochemistry of a-C:H:Si:O and the resulting tribological behaviour. A correlation with previously published, state-of-the-art molecular dynamics simulations will be discussed. Second, I will discuss our recent investigation of the mechanochemistry of a well-established, yet not fully understood antiwear additive, zinc dialkyldithiophosphate (ZDDP). The origin of the excellent antiwear performance of ZDDP in commercial lubricants constitutes a long-lasting open question. In automotive application of ZDDP, the large amounts of phosphorus, sulphur, and zinc in ZDDPs can block filters and lead to catalyst poisoning and subsequent degradation affecting the emission quality over the operating life of an engine. Consequently, the development of novel metal-free antiwear additives, which perform as well as, or even better than ZDDP and produce lower or zero levels of sulphated ash, phosphorus, and sulphur by-products, is deemed necessary. This motivates fundamental studies to elucidate the origins of the effectiveness of ZDDPs. We recently shed light on the mechanochemistry of ZDDP by developing a new methodology based on AFM [2], which allowed the formation and growth of ZDDP tribofilms to be visualized and quantified in situ, in single asperity contacts with nanometer-scale spatial resolution. The experimental results provided new insights into ZDDP tribofilms' growth mechanism and kinetics and addressed multiple conflicting hypotheses in the literature concerning the function of the antiwear films formed by ZDDP upon sliding.

[1] Koshigan, K. D.; Mangolini, F.; McClimon, J. B.; Vacher, B.; Bec, S.; Carpick, R. W.; Fontaine, J., *Understanding the hydrogen and oxygen gas pressure dependence of the tribological properties of silicon oxide-doped hydrogenated amorphous carbon coatings*. *Carbon* 2015, 93, 851-860.

[2] Gosvami, N. N.; Bares, J. A.; Mangolini, F.; Konicek, A. R.; Yablon, D. G.; Carpick, R. W., *Mechanisms of antiwear tribofilm growth revealed in situ by single-asperity sliding contacts*. *Science* 2015, 348 (6230), 102-106.

### ***Tribological properties of cu alloys by atomistic simulations***

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Synthesis of wear resistant materials is critical for a wide range of engineering applications, including engines, orthopedics, electrical contacts, and general bearings. It has been shown that wear as low as ~100 nm/hour (so called ultra-mild wear) can be achieved in metals that during sliding develop a tribolayer consisting of nanocrystalline (nc) grains. In such nc layers, mechanisms of deformation and wear are often different than in polycrystalline samples due to the presence of a large volume fraction of grain boundaries (interfaces). Interfaces can be also introduced artificially into the coating, for instance by creating multi-layer materials. In this study molecular dynamics simulations were employed to discover the role of grain boundaries and interfaces in deformation and wear of Cu and Cu-Ag alloys. We report the dependence of these phenomena on grain size, and on concentration of Ag impurities. For pure Cu we find that there is an optimum grain size that minimizes wear due to the coupling of the grain size (intrinsic size effects) to the contact size (extrinsic size effect). Dissolved Ag is found to have a pronounced effect on strength of Cu-Ag alloy because Ag impedes dislocation nucleation and glide – even in cases where Ag is segregated to grain boundaries. Multilayer Cu-Ag systems were also considered and shown to exhibit a significant amount of plastic strain recovery. The origin of this recovery and its implications for tribological properties will be discussed.

### ***A general, predictive model of friction in metallic contacts***

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Engineering design of sliding metallic contacts is generally guided by the rule of thumb that increased hardness leads to lower friction. Recent molecular dynamics simulations performed by our group have

demonstrated that this relationship is more accurately described as correlation than rather causation. Our work shows that both these macroscopic observations have their roots in the same atomistic mechanisms, namely accommodation of stress through grain boundary sliding as opposed to dislocation mediated plasticity. This result has been confirmed by a series of experiments, and has allowed us to develop a general, predictive model for friction and wear in metallic contacts. We will present the details of this model, including physics-based predictions of applied load thresholds, and the resulting friction and wear coefficients. Experimental results that confirm the model predictions will also be presented. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

### ***Mechano-chemistry of fracture and plasticity***

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The role of chemistry in mediating mechanical performance is widespread but challenging to model for various reasons. We highlight here three efforts in this general area where the application of mechanics, chemistry, and transport, determines the time-dependent mechanical response of a material. Then, a new multiscale algorithm for long-time simulations of mechanical problems with chemical transport is presented and discussed. We first discuss a new nanoscale mechanism wherein H accumulates at nanometer scales around any pre-existing crack tip, which shuts off the crack tip dislocation emission and thereby eliminates crack blunting and suppresses ductile failure modes; fracture then occurs by cleavage through the brittle H-rich region and the process is self-sustaining through continual H transport to the crack tip region. We then discuss structural transformations in Magnesium, and how chemistry may be able to affect these transformations and help improve Mg ductility. We then discuss how time-dependent charging/discharging in amorphous Li-Si battery materials affects the plastic flow in these systems. Finally, we present a multiscale algorithm that couples direct accelerated molecular dynamics (AMD) of extended defect evolution to a diffusion model of point defect flow into and out of the defect, which captures the long spatial and temporal scales of point defect motion in the presence of the internal stress fields generated by the evolving defect. The algorithm is applied to study vacancy absorption into an edge dislocation in aluminum where, under a sufficient driving stress and vacancy supersaturation, vacancy accumulation in the core leads to nucleation of a double-jog that then operates as a sink for additional vacancies; this corresponds to the initial stages of dislocation climb modeled with explicit atomistic resolution. The method is general and so can be applied to many other problems associated with nucleation, growth, and reaction due to accumulation of point defects in crystalline materials.

## 4 Posters

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### ***Deformation of sodium borosilicate glasses under load using molecular dynamics simulations***

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In this study we present the results of nanoindentation and isostatic compression simulations of sodium borosilicate glasses using Molecular Dynamics, alongside experimental results obtained by Raman spectroscopy. For nanoindentation, three glasses with varying sodium content were simulated both in their pristine form, as well as a “disordered” one, which is analogous to the real irradiated glass and exhibits a swollen and more depolymerized network. The results indicate a very low increase of coordination of the silicon atoms, in contrast to boron and sodium. Densification occurs by the decrease of free volume and takes place in regions rich in glass formers. On the contrary, we observed evidence of high shear flow around sodium atoms. In the compression simulations, the pristine forms of the glasses were brought to a pressure of 20 GPa and then decompressed again. We found that the amount of free volume has a major influence on the amount of densification, alongside the percentage of three-coordinated boron. At the same time, sodium creates soft regions in the glass that can be more easily compressed. The results are then compared to Raman spectra collected on the imprint marks of experimentally indented borosilicate glasses.

[1] D.A. Kilymis and J.-M. Delaye, *J. Non-Cryst. Solids* 401 147 (2014)

[2] D.A. Kilymis and J.-M. Delaye, *J. Chem. Phys.* 141 014504 (2014)

[3] D.A. Kilymis, J.-M. Delaye and S. Ispas, *submitted for publication*

### ***Multiscale study of the mechanical behaviour of nickel-based alloys***

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Recent developments in materials engineering such as the production of new generation superalloys that exhibit excellent high temperature mechanical strength have stimulated interest in the comprehension of the underlying atomistic effects, which are surprisingly poorly understood because of the complex chemistry invariably involved at the nanoscale. The ‘Learn on the Fly’ [1] (LOTF) approach is a multiscale QM/MM coupling scheme that allows these kind of ‘chemo-mechanical’ processes to be modelled with ab initio precision. The main goal of this project is understanding the motion of dislocations neighbouring the  $\delta$  phase interface at the atomistic level, in particular the effect of substitutional impurities such as Rhenium atoms on diffusion processes. Detailed convergence tests reveal that accurate forces at a dislocation core can be achieved using only modest-sized clusters for the embedded QM calculation, and Rhenium impurities and vacancies can be embedded with average-sized clusters, since their effect on both QM forces and local chemistry is short-ranged [2].

[1] G. Csanyi, T. Albaret, M. Payne, and A. De Vita. *Phys. Rev. Lett.*, 93 175503 (2004)

[2] F. Bianchini, K.N. Goswami, A. Mottura, J.R. Kermode, A. De Vita, *in prep.*

### ***A uniaxial deformation study of polystyrene-silica nanocomposite materials using molecular dynamics–finite element coupling approach***

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Polymer nanocomposite materials have obtained enormous attention in academic and industrial fields over last five decades. Polymer nanocomposite systems are produced typically by adding nanoscale (1-100 nm) inorganic fillers into polymer matrix. Nanoparticle enhancement effect contributes to an enormous performance improvement of polymer nanocomposites due to the presence of a large amount of interfacial region where polymer chains undergo conformational changes and deformations at the nanoscale. It is still a challenge to understand the mechanism of nanoscale enhancement to the interfacial structure and the mechanical behavior of nanocomposites from a microscopic perspective. A molecular dynamics-finite element (MD-FE) hybrid approach has been recently developed to simulate soft matter systems. In this work, the hybrid method is applied to investigate the mechanical properties of coarse-grained polystyrene/silica nanocomposites. The effect of nanoparticle properties on mechanical performances of polymer nanocomposites has been studied. The normal stress distribution and the Young's modulus of nanocomposites have been calculated during the uniaxial deformation. In addition, polymer properties near to nanoparticles, including end-to-end distance, radius of gyration and chain orientation parameters, have been estimated to compare with the bulk properties. It is observed that with the decrease of particle size, the stiffness of polymer nanocomposites increases. The MD-FE coupling computations provide a profound understanding in a microscopic viewpoint about the structure-property relation of polymer nanocomposites, which is helpful to design novel nanocomposite material with excellent performances.

[1] M. Rahimi, H.A. Karimi-Varzaneh, M.C. Böhm, F. Müller-Plathe, S. Pfaller, G. Possart, and P. Steinmann, *J. Chem. Phys.* 134, 154108 (2011).

[2] S. Pfaller, M. Rahimi, G. Possart, P. Steinmann, F. Müller-Plathe, and M.C. Böhm, *Comput. Methods Appl. Mech. Eng.* 260, 109 (2013).

[3] S. Liu, A. Gerisch, M. Rahimi, J. Lang, M.C. Böhm, and F. Müller-Plathe, *J. Chem. Phys.* 142, 104105 (2015).

### ***A framework for highly parallel ml-augmented qm/mm dynamics***

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Very often simulating systems and processes found in nature requires a multiscale QM/MM modelling approach. QM methods are necessary to correctly capture complex chemical phenomena occurring in small portions of the system. A classical MM approach is instead sufficient to describe the remainder of the system, whose extent is often far too large to allow a full-QM representation. Crucially, chemically "interesting" situations determining the activation of QM treatment of an atomic neighbourhood take place along a dynamics only at certain time and space domains of the system trajectory that cannot be known a priori. Furthermore, information-efficient Machine Learning methods could recognise chemical situations similar to previously encountered ones, allowing to predict QM-accurate energies and forces at a negligible cost when compared to ab initio calculations. With these specifications, the emerging scenario consists of a full QM zone made up of smaller time-evolving QM regions of moderate sizes. We propose an ensemble parallel QM/MM architecture which makes optimal use of the available computational power by partitioning the QM region into multiple smaller parts, concurrently evaluated by separate QM engines and appropriately load balanced by means of a newly developed partitioning algorithm. Together with a criterion to estimate the prediction error in a ML regression scheme, the flexibility given by the new architecture could be used to incorporate ML into QM/MM methods. QM force prediction would be used to accelerate QM calculations in local atomic configurations belonging to already probed regions of phase space, and a set of QM engines calculating fresh information where ML regression is not reliable.

### ***Wear at the asperity level: an atomistic viewpoint***

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Tribological problems are particularly difficult to comprehend. Different physical mechanisms (including the environment, plastic deformation, third body interactions, phase transformations, recrystallization) interact at disparate length and time scales. Here, we will present some of our recent attempts to understand the origins of wear mechanism at the atomistic level. Macroscopically, the wear process, in terms of debris formation, is well described by the well-known Archard model [1]. As suggested, the wear rate is linearly proportional to the ratio of the applied force to the material hardness with a constant factor called wear coefficient which represents the probability of wear debris formation. This coefficient is the most important yet least understood parameter in the field of tribology. Since the physical origins of the debris formation process are still unclear, this coefficient cannot be estimated theoretically and must be only determined experimentally. In order to understand the physical origins of the debris formation process, we have performed a systematic set of molecular dynamics simulations employing a new family of interatomic potentials. These potentials allow us to independently modify physical properties such as hardness and surface energy where other parameters remains constant. Using that, we will discuss different wear mechanisms at the asperity level ranging from a gradual smoothing to a debris formation. Additionally, we elaborate the steady-state sliding regime in terms of frictional force, debris size and surface roughness and explore several influencing parameters such as applied load, sliding velocity and inter-facial adhesion [2]. The proposed framework opens up a new research path to implicitly model and explore the wear process and revisit classical models.

[1] J. F. Archard (1953) *Journal of Applied Physics*

[2] R. Aghababaei, D. H. Warner and J.F. Molinari (2015) *to be submitted*

### ***Molecular modeling of liquid/liquid interfaces: learnings for lubrication problems***

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Molecular modeling of fluid/fluid interfaces receives continued attention in industrial research. In the petroleum industry, applications range from multiphase flows in pipelines, to oil recovery, and oil spill remediation. The focus lies on interface properties, such as the interfacial tension, and attempts have been made to utilize molecular modeling tools to understand the role of added surfactants in lowering the interfacial tension. Using high-performance computing calculations of interfacial tensions have become feasible on atomistic level. Beside the forcefield quality one of the main challenges remains, however, namely the determination of the adsorption isotherm which provides the partitioning of surfactants between the bulk solution and the interface. It is computationally infeasible to directly sample such partitioning using atomistic Molecular Dynamics (MD) simulations. A potential solution lies in the combination of molecular-thermodynamic theories with MD methods. We will demonstrate the capability of such an approach on a model system that consists of non-ionic polyethylene glycol (PEG) surfactants at a water/heptane interface. We utilize a molecular-thermodynamic framework by D. Blankschtein et al. (Langmuir 1992, 1999) and combine it with MD simulations to determine the partitioning of PEG surfactants between bulk water and the water/oil interface which allows prediction of surfactant interface coverage at given surfactant bulk concentration. The latter is the actual experimental control parameter. A second outcome of such an approach is the predictability of competitive adsorption in surfactant mixture solutions and the effect on interfacial properties. Learnings from such modeling approaches of liquid/liquid interfaces might be useful for lubrication purposes. For example, modeling organic friction modifiers dissolved in engine oil underlie similar challenges. The aim is to predict the adsorption

behavior of such compounds on solid substrates, such as steel. We propose a molecular-thermodynamic model in combination with MD which allows prediction of the surface coverage and friction coefficient at given concentration of organic compounds dissolved in engine oil.

### ***Modeling afm adhesion measurements as adhesive elastic contact***

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Understanding adhesion forces in dry contact is of particular importance for the study of many technical and biological systems. Even in their simplest manifestation -- the pull-off force necessary to break the contact between a nano-scale indenter and a rough surface -- they are poorly understood. We model a stiff spherical indenter on an elastic rough substrate interacting with an empirical atomic-scale interaction potential. The model has been validated against a series of AFM pull-off measurements performed with silicon tips with tip radii varying between 14 nm and 100 nm on an ultra nanocrystalline diamond (UNCD). Without any fitting parameters, we find good agreement between the experiment and our simulations. We analyse the link between the distribution of pull-off forces and the statistical roughness properties of the substrate. By comparing measured to simulated distributions, additional statistical information about short-wavelength surface features, too small to be measured directly, can be obtained.

### ***Shear flow of confined lubricants between surfaces with slipping and sticking domains***

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Lubricated contacts must cope with increasingly severe conditions, which lead to a boundary lubrication regime featuring nanometer-thin oil films. Under this state of severe confinement, the fluid shows deviations from its bulk behavior, such as density layering, viscosity enhancement, and slip at the wall-fluid interface. Molecular Dynamics (MD) can be used to quantify the behavior of nanometer-thin fluid films, which is difficult to access through experiments under highly loaded conditions. We here investigate the shearing of a lubricant confined between two parallel surfaces with slipping and sticking domains. In contrast to simple Couette flow for homogenous surfaces, the velocity profiles in the heterogeneous system curve to ensure a constant flow despite slip variations in the shearing direction. Local slip can still be quantified through a slip length extracted from small-scale MD simulations with homogeneous surfaces. We find linear pressure variations of the order of the external pressure along the shearing direction, indicating that the lubricant flow is both shear- and pressure-driven. Finally, we modify the well-known continuum Reynolds equation to include slip from small-scale MD simulations, and solve it analytically. This expression reproduces perfectly all aforementioned phenomena for a wide range of operating conditions and oil film thickness down to the nanometer scale.

### ***Chain ends and the ultimate strength of polyethylene crystals***

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Understanding the microscopic mechanisms of yielding in oriented polymer fibers is a long outstanding problem in polymer mechanics. While advances in polymer processing have produced highly ordered polyethylene (PE) fibers with substantial tensile strengths between 4-7 GPa, these values are far less than the theoretical ultimate strength of 20-30 GPa, where PE chains fail due to C-C bond scission. This

reduction in strength is caused by the presence of defects within the fiber's crystal structure. The simplest defects are chain ends – i.e., finite length of polymer chains. Chain ends allow a fiber to yield by chain slip, without scission of covalent bonds. However, chain ends may also lead to strain localization and allow bond scission at much lower applied stresses. Here we present extensive molecular dynamics (MD) simulations of crystalline PE fibers subjected to uniaxial tension. The fibers are fully aligned crystals constructed from chains of finite lengths, which span three orders of magnitude ( $10^1$ -  $10^4$  monomers). Chains always yield by chain slip at stresses  $\sim 6$  GPa. We observe chain slip is facilitated by the nucleation of 1D dislocations along the chains. To investigate, we parametrize a Frenkel-Kontorova (FK) model for a finite chain in the periodic potential of the surrounding crystal. Dislocations in the FK theory are in quantitative agreement with MD. We find crystal strength is limited by the stability of the crystal to dislocation nucleation at chain ends.

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