Annual Report 2003

CSCS

Swiss National Supercomputing Centre

Accelerating Scientific Discovery

Edited by Angelo Mangili (http://www.cscs.ch/∼amangili), CSCS.

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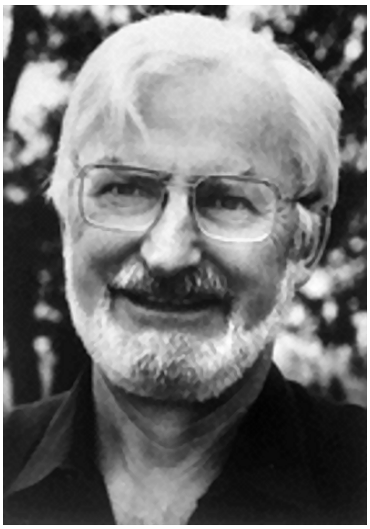
Preface



2003 was a year of fundamental changes at CSCS. The new organizational setting as an autonomous unit of ETH Zurich led by performance mandate and global budget are the most visible expressions of these changes. In this framework, the new CSCS management under the direction of General Manager Dr. Marie-Christine Sawley has the operational freedom and responsibility to realise the strategic guidelines set by the CSCS Steering Board for developing and establishing a world-class high-performance computing centre.

In March 2003, former director Prof. Michele Parrinello chose to resign from this position in order to concentrate on his research as a professor of ETH Zurich in computational science. The ETH Board commissioned a taskforce to define the future direction, organisation and framework of the centre.

By the middle of the year, Marie-Christine Sawley had taken over the position of executive manager of CSCS. She worked out and proposed a business plan for CSCS to the working group, which outlines the scientific and technological strategy, the budget and the management that will enable CSCS to become a leading-edge HPC centre of international scale. The final proposals by the working group, which were based on the functioning principles of the FLAG institutions of the federal administration, were accepted by ETH Board and ETH Zurich by the end of 2003 and took effect in 2004.

Whilst these fundamental changes were being planned and unfolded, CSCS continued to serve the Swiss scientific community with its outstanding technical services and developing capabilities. The results of these activities are collected in the report at hand.

It is now the responsibility of the umbrella institutions, ETH Zurich and ETH Board, to secure adequate and continuous future funding for a sustainable development of the centre. Under such conditions, I strongly believe that the quality of the science that was enabled by CSCS during the last year together with the new organisation and direction that have been established, bode extremely well for what the centre will be able to achieve in the future.

Dr. Heinrich Rohrer
Chairman of the 2003 CSCS working group

Word from the General Manager

2003 saw the preparation and acceptation of a major plan, aiming at positioning the CSCS as a key partner for supporting excellence in research and development of knowledge at the frontiers of science needing high performance IT capabilities. As a result of the recommendations made by the working group piloted by Dr. Heinrich Rohrer, the Centre started to reinforce its capacity to serve the national scientific community, to define and to implement the next generation of infrastructure - both hardware and software- that will enable further scientific discovery, both on a national and international scale.

As General Manager of the CSCS, I am very pleased to present you with an outlook on the scientific projects and on the work accomplished during this transition year. Based on this rich portfolio, and stimulated by the excellent experience with our present strategic partners the Computational Science Laboratory of ETH Zurich and Meteosuisse- close collaborations with scientific communities from the ETHs, the Universities and Universities of Applied Science, research institutions and partners from the private sector, will continue to develop, anchoring the CSCS in the ever evolving landscape for research and education, with specific skills and value added services.

Since the beginning of 2004, the CSCS has become an autonomous unit of the ETH Zurich, working under global budget and performance mandate. The winter months of 2004 saw the indispensable changes take place that would make this new important step a reality: the CSCS Steering Board and Scientific Advisory Board were nominated, and a new internal structure was implemented at CSCS. This development necessitates investing both in people competences and IT infrastructure, acting as stimulant for young talents.

This exciting growth phase will be accomplished in close synergy with our partners in the Italian speaking part of Switzerland, by contributing to a cluster of complementary competences.

Marie-Christine Sawley,
General Manager

Partners and Projects

VA Tech Hydro

Analysis of 3d Unsteady Free Surface Flows in Pelton Turbines: Advanced Numerical and Experimental Investigations

The objective of this project is to develop an advanced method for flow simulation in Pelton turbines. Several water jets impinging the runner buckets ensure the motion of the impulse turbine, leading to complex characteristics of the flow, i.e. 3 D turbulent, 2 phases and unsteady. A newly developed CFD commercial code will be adapted and validated to perform such a flow simulation. An extensive experimental validation will be carried out through an innovative technique aimed to visualize the jet impingement and its complex interaction with the runner buckets. Furthermore, substantial work will be performed to develop modern tools for post processing CFD and experimental data. The result of the project will definitely allow the industrial partner to significantly improve the design process of Pelton turbines.

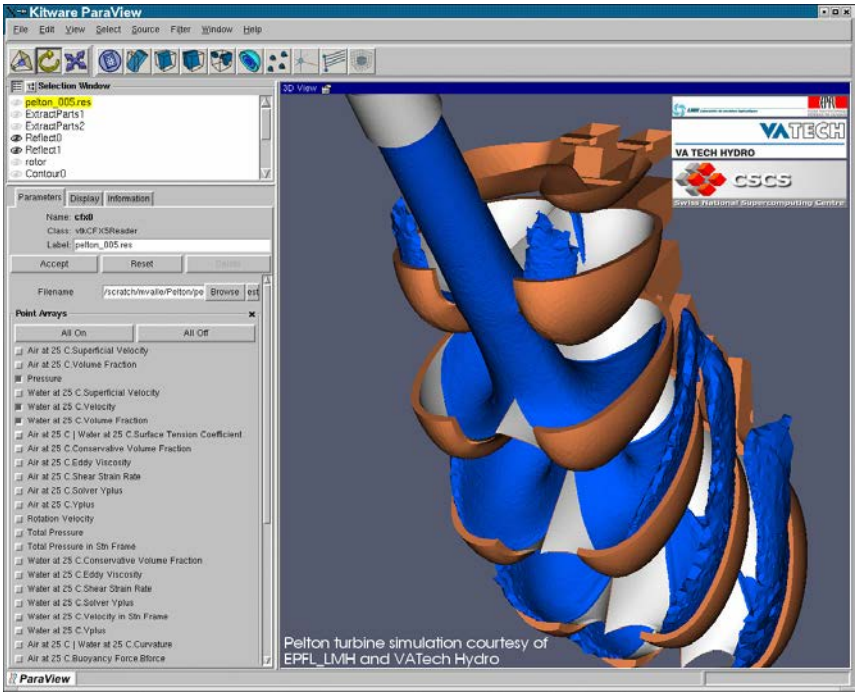


Figure 1: *The water jet is shown leaving the injector, impinging the buckets at different angles and positions, and the water sheets being evacuated on the sides.*

Project and Funding Partners includes: VA Tech Hydro SA; Ecole Polytechnique Federale de Lausanne, Laboratory for Hydraulic Machines; Swiss National Supercomputing Centre and the Innovation Promotion Agency (KTI/CTI) of the Swiss Federal Office for Professional Education and Technology

Contact: J.M. Favre

CERN: High Energy Physics community

The Swiss Tier 2 of the CERN LCG Project

The European High Energy Physics community is building the Large Hadron Collider (LHC) - the worlds biggest accelerator at (CERN) in Geneva[1]. Challenges to be faced by physicists are unprecedented: data collected by these experiments will allow for exploration of new frontiers of the fundamental laws of nature, like the Higgs mechanism with possible discovery of the Higgs boson.One of the greatest challenges of the LHC project will be the acquisition and analysis of the data. The equivalent data volume is between 100 MByte/sec and 1 GByte/sec. Each experiment is expected to collect 1 PByte of raw data per year. 2000 physicists per experiment contribute to the development of hardware and software and they expect to have almost instantaneous access to the data and to a set of up-to-date analysis tools.

The goal of the LCG (LHC Computing Grid) project is to meet these unprecedented computing needs by deploying a worldwide computational grid service, integrating the capacity of scientific computing centres spread across Europe, America and Asia into a virtual computing organisation. Switzerland, as member state of CERN, actively participates in the LHC project as a whole. The CHIPP group reunites the University laboratories in Switzerland involved in scientific analysis and development of the data produced by the experiments of the LHC. The CSCS has teamed up with CHIPP since 2003 by establishing the first prototype of a LCG Tier-2 cluster.

Contact: G. Volpato

European Projects:

EUROGRID

The main objective of EUROGRID was to build a European GRID infrastructure that gives users a seamless, secure access to High Performance Computing resources and that allows progress in computational science in Europe. In three years of activities this project has demonstrated the suitability of GRIDs for selected scientific and industrial communities, addressed the specific requirements for these communities, and highlighted the benefits of using GRIDs. CSCS contributed directly in the HPC Research GRID and in the Meteo-GRID work packages of the project. The first work package consisted in establishing a European GRID network of leading High Performance Computing centres from different European countries. The second work package's goal was to exploit the established GRID in order to deliver on-demand weather forecast services.

Grid computing is emerging as an effective approach to solve large-scale problems that involve the cooperation between different entities and can require high-performance computing resources. The grid paradigm is particularly suitable for weather forecast applications that need observation data inputs from different sources and, depending on different parameters such as forecast time and resolution, demand a specific computing power.

For this purpose, CSCS developed the LM plug-in application that extends the basic functionality of the standard EUROGRID software in order to provide an ASP solution for weather forecasts. This application allows the performance of high-resolution short-range weather forecasts with the

[1] CERN Large Hadron Collider (http://www.cern.ch/lcg)

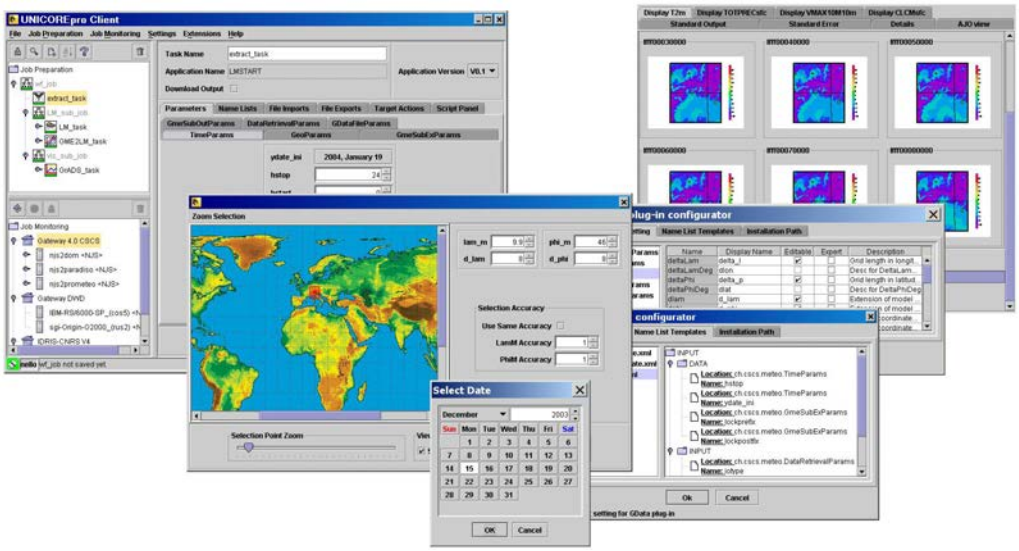


Figure 2: *Overview of the graphical user interface of the LM plug-in.*

relocatable nonhydrostatic Lokal-Modell (LM) of DWD in an UNICORE based grid. In particular, the LM plug-in is a Java application available as a UNICORE client plug-in that defines an abstract model for the weather forecast process and uses this model to build, configure and execute a job in an UNICORE grid.

Performing a weather forecast with LM is a complex process that involves various activities such as derivation of the topographical data set for the selected geographical domain, extraction of initial and lateral boundary data sets for LM, interpolation with GME2LM, numerical weather prediction with LM, and final post processing and/or visualization of forecast products. Each activity has different requirements respect to software and hardware resources. For example the topographical data in the first step consist of high resolution information about orography, land fraction, soil type and vegetation that are derived from a large data set of about 7 GBs. This is not an expensive operation in terms of computing power but the availability of a global topographical data set has to be guaranteed. On the other hand the execution of LM is a computationally demanding task that requires high performance computing facilities in order to produce a weather prediction in a reasonable amount of time. Indicatively, a typical 48 hours forecast with LM for a domain of 300 x 300 grid points and 40 vertical layers needs up to 60 x 1012 floating point operations. Therefore, the UNICORE paradigm is perfectly suitable for this kind of problem since it allows the selection of the most appropriate architecture for the specific task and uses heterogeneous resources in a collaborative way in order to produce the final results.

The final review meeting for the EUROGRID[2] project was held on the 22nd January 2004 in Paris. This was the occasion to show the results of three years of activities and the latest development carried out by the project consortium. The project received very good comments from the reviewers, who particularly appreciated and underlined the technical value of the work done in the further development and improvements of the GRID middleware.

Contact: M. Ballabio

[2] EUROGRID: Application Testbed for European GRID computing (http://www.eurogrid.org)

ENACTS

The ENACTS[3] (European Network for Advanced Computing Technology for Science) project aims to evaluate future trends of the way in which computational science will be performed and the ensuing pan-European implications. The project activities were organized around three phases: a set of preliminary technology studies and surveys, a deployment of a grid test bed and users'needs survey, and a final dissemination phase.

For the study phase different reports such as "GRID Service Requirements", "HPC Technology Roadmap", "Data Management", "Distance Learning and Support" and "Software Efficiency and Re-usability" were produced . CSCS contributed to the preliminary study activities with the "Grid Enabling Technology" report written together with the Foundation for Research and Technology-Hellas (FORTH) in Greece. All the reports are now publicly available on the ENACTS web site.

During the 4th project meeting hold in Prague on the 11-13 March, the ENACTS pan- European Metacentre was presented as applications demonstrator. In particular the work was base on QCDGrid (Quantum Chromodynamics) software, Globus middleware and XML technologies for meta-data representation and cataloguing. The demonstration test bed aimed to draw together the results from all of the technology studies and evaluate their practical consequences for operating a pan-European metacentre and constructing a best-practice model for collaborative working amongst individual facilities. The project has now entered its final phase and in the next year the users' needs survey will be produced and all dissemination activities will take place. In order to disseminate the project results, the ENACTS consortium will organize a workshop for users of molecular simulation techniques, one of the core user groups of computational science.

Contact: N. Nellari

PRISM

PRISM[4] is a major EU-financed program for integrated earth system modeling with a goal to develop the pilot European climate modeling software infrastructure, enhance the efficiency of earth system modeling in Europe and pave the way for the establishment of a European Climate Computing Facility.

The expected product will be a flexible, efficient, portable, and user friendly community infrastructure for earth system modelling and climate prediction. To reach this objective, PRISM will:

- Create a European service and management infrastructure for developing, coordinating and executing a long-term programme of Europe-wide, multi-institutional climate and Earth System simulations.
- Develop a European system of portable, efficient and user-friendly Earth System / climate community models and associated diagnostic / visualization software under standardised coding conventions that can be accessed by all European scientists.

As a result of the PRISM project, the scientific community involved in Earth system modelling in Europe will adopt a common software for model development, model diagnostics and visualization. This new approach will allow easy exchange of codes and easy execution of ensembles of

[3]ENACTS: European Network for Advanced Computing Technology for Science (http://www.enacts.org)
[4]PRISM: PRogramme for Integrated earth System Modelling (http://prism.enes.org)

climate simulations for different model configurations[5].

CSCS's contribution in the frame of this challenging project, was to assess the state, the trends, and the future of High Performance Computing (HPC) in relation to the development of PRISM components. This investigation is motivated by the need for early identification of the best suited programming languages and paradigms as well as parallelization strategies targeting the reduction of porting and maintenance efforts of the software product over different platforms, as well a good performance and scalability on leading edge HPC facilities over the years to come[6].

CSCS also substantially contributed to the definition of the PRISM Software Developer's Guide as the reference handbook describing the development practices, standards, and conventions recommended for the development of PRISM base software and components. The scope of this document includes any issue related to process, conventions, and standards in the design, implementation, and documentation of any software that will be developed in the frame of the PRISM project under the consideration of portability, sustained performance and ease of use[7].

Contact: A. Mangili

[5] PRISM System Spec. Handbook (http://prism.enes.org/Results/Documents/Handbook/handbook.v.1.0.3.pdf)
[6] PRISM REDOC III.2 (http://www.cscs.ch/~amangili/papers/PRISM_HPCtrends.pdf)
[7] PRISM ARCDI II.5 (http://www.cscs.ch/~amangili/papers/PRISM_SEguide.pdf)

HPCN Technology and Resources

During this very important transition year the two major driving forces for the development of the CSCS High Performance Computing and Networking (HPCN) technologies and related services have been to continue delivering the high quality support to our national end-user community and to prepare for the major upcoming technology upgrades in 2004/2005 according to the new CSCS development plan. The permanently growing needs of our end-user communities, and a further reinforced emerging trend towards multi-physics and multi-scale application integration have driven our daily operational efforts in managing the very high and heterogeneous loads on both the parallel vector processing (PVP) NEC SX-5 and the massively parallel processing (MPP) IBM SP-4 supercomputers. Furthermore, the major upgrade projects of our data management services have been carried out.

The data moving needs posed by HPC-systems have always required custom-enabled, supercomputing-specific data management enhancements (both for storage and networks) at the level of the architecture and software. Ever-higher data densities (for both disk and tape) and the permanently decreasing market cost of raw storage are however not being offset with corresponding data moving sustained performance improvements. This ”divergence” issue, which is one of the biggest challenges for the mainstream market, is obviously even more critical for supercomputing centers. One of the major issues for the HPCN-centers within the time horizon of 2010 will be the integration of the heterogeneous supercomputers with the data management solutions and ”hiding” the complexity introduced by the huge number of heterogeneous subcomponents. The CSCS data management upgrade project should set a base for future work of this kind and above all enable a smooth integration of the new CSCS supercomputing systems.

In order to achieve its most important goal of making the most adequate HPCN-resources available (systems, networks, data management and storage) to the CSCS end-users community in a reliable, performing and easy-to-use fashion, the CSCS HPCN production environment has to be permanently developed and optimized based both on the continuous and pro-active prospection and evaluation of new HPCN-technologies, as well as on the permanent assessment of the current and future users’ requirements. To this end, a significant comprehensive analysis of the supercomputing technology and market trends has been initiated in the reporting year with the objective to provide the vision and strategic objectives that on a longer term will serve as a framework and fundament for the permanent detailed CSCS technology development planning process. The current ”renaissance” of the supercomputer architecture work both in the US and in Japan set a very positive and interesting environment for the CSCS upgrade projects in the nearest future.

Dr. Djordje Maric
CTO and Head of HPCN Service Division

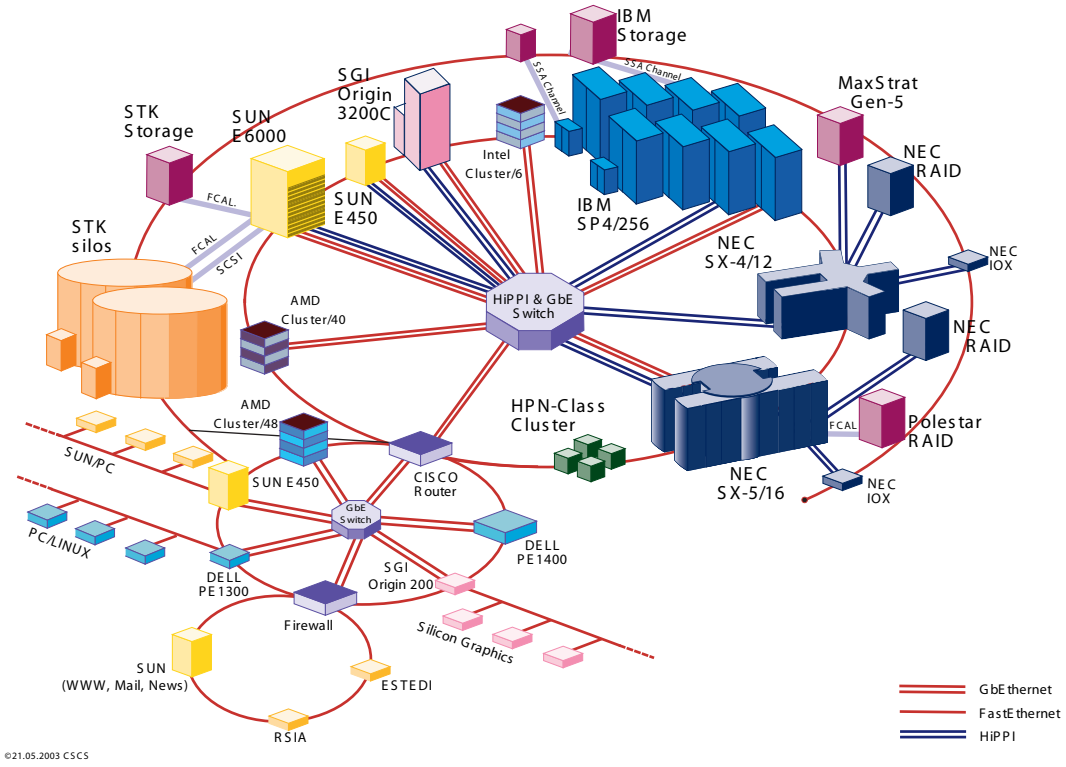


Figure 3: CSCS HPCN resources at a glance.

HPCN Resources

In 2003, CSCS offered supercomputing services to the national User community on the following architectures (see Figure 3):

- Parallel Vector Processing (PVP), with a NEC SX-5 of 16 CPUs, totaling a theoretical peak performance of 128 GFlops and 64 Gbytes shared memory, running under Super-UX with NQS scheduler. The network connection is provided via GigabitEthernet, HiPPI and FastEthernet.
- Massively Parallel Processing (MPP), with 8 IBM Regatta p-690 SMPs of 256 CPUs total, 768 GBytes of main memory, totaling a theoretical peak performance of 1.38 TFlops. The SP frames are tightly coupled and switched by a Double Colony system in order to provide a Parallel Environment with a Global Parallel File System of 4 TB. The overall system run on AIX with LoadLeveler job management system. The system is complemented by 2 Nighthawks (Power3 nodes, total of 32 CPUs and 32 GBytes main memory) with a peak performance of 48 GFlops.
- In addition, a small loosely coupled HP cluster has been offered as a complement for throughput computing using mainstream Independent Software Vendor (ISV) packages.

Given the importance of the close integration of supercomputing with data management, CSCS has been offering its Users an application-oriented, integrated computing environment linked with very fast internal network connections. The data management and archiving services are based on the SAM-FS Hierarchical Storage Management software, which handles an archived raw data volume currently in excess of 250 TB. A major upgrade of the CSCS Archive facility was started to

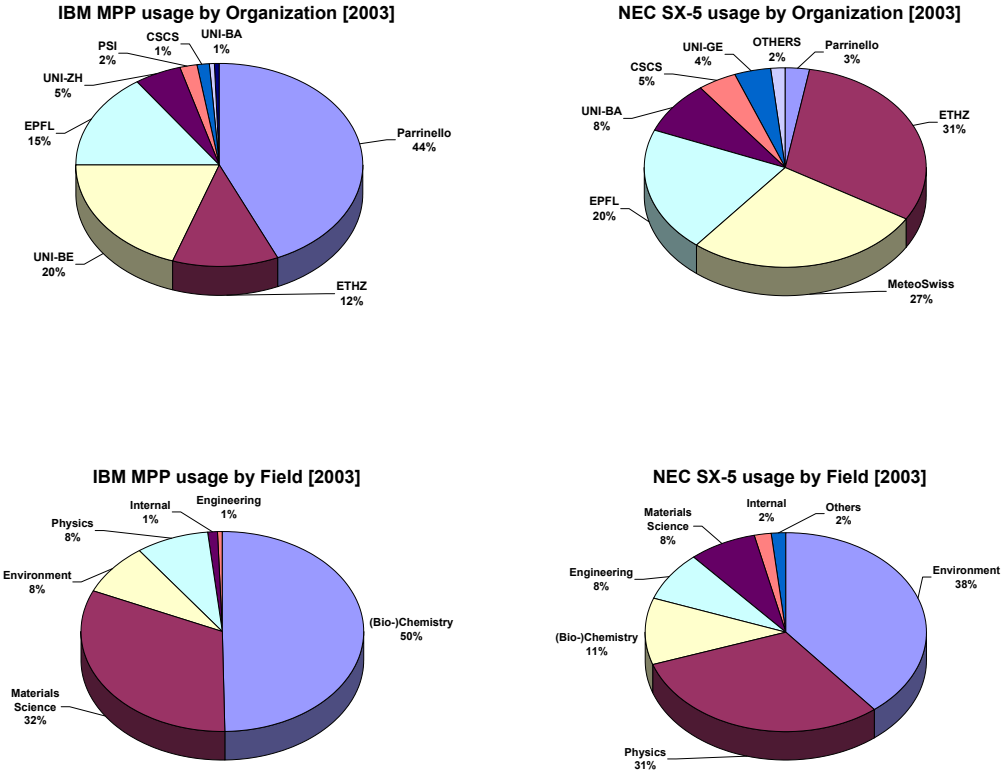


Figure 4: *CSCS HPC resource usage statistics by fields and by organizations for 2003.*

allow Users to benefit from higher archive access performance and increased service availability.

The core architecture of the high-performance production network is based on HiPPI and GigabitEthernet technologies with standard protocols. The deployment of the latest-available GigabitEthernet standard was launched during the reporting period, with the introduction of the routing equipment and two GigabitEthernet switches interconnecting the MPP, the PVP, the HP cluster, the Archive and the Front-end Environment. The CSCS local area network is integrated into the Swiss Academic and Research Network WAN (SWITCHlambda) ensuring the connection to CSCS's end-Users.

The HPCN environment is constantly protected by a global security infrastructure that provides a suitable security service level for the national User community that comprises academia, federal government agencies and industry.

User Community

The Swiss CSCS users community is widely distributed over the two Swiss Institutes of Technology and the Cantonal Universities (see also Fig. 4). The group of Prof. M. Parrinello (Computational Science, ETHZ Chemistry Department) is the main User of the MPP system. The CSCS Research Committee, composed of prominent scientists representing all major User application fields as well as Swiss Universities using CSCS services, reviews Large User Projects (LUP) and

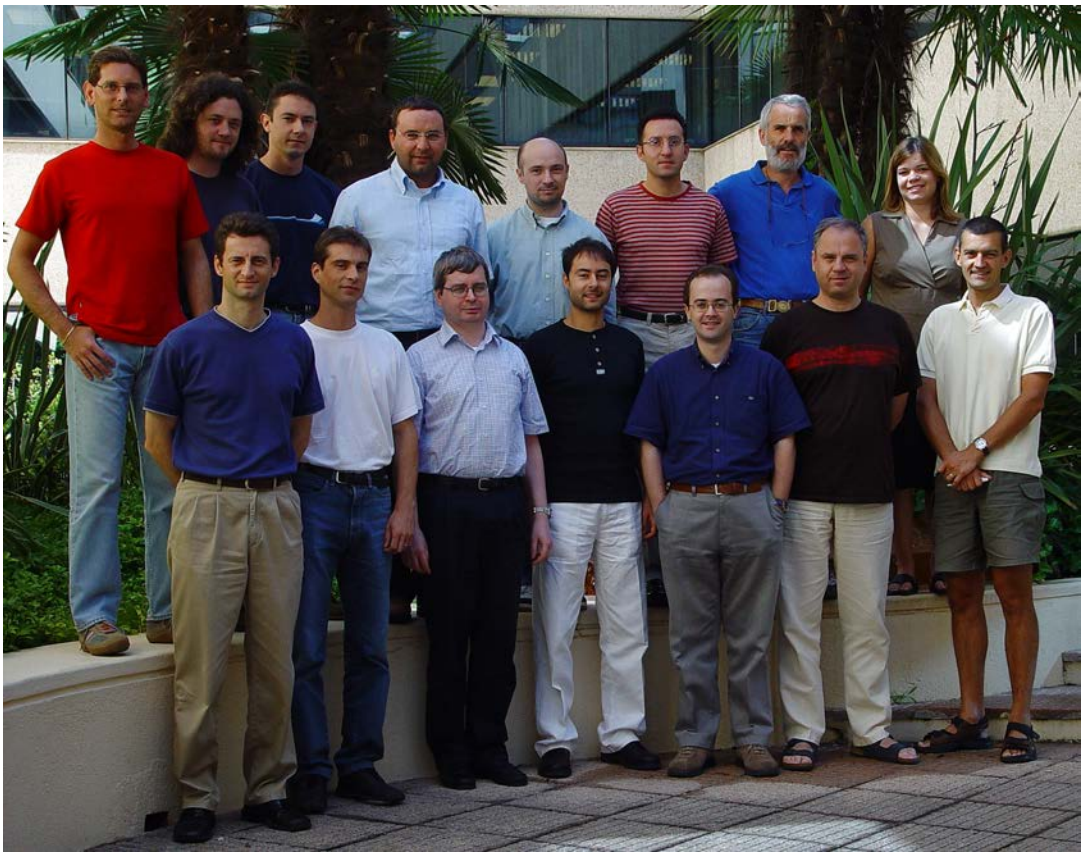


Figure 5: The team of the 2003 HPCN Service Division. Not present: D.Maric, L.Bacchetta, G.Gobbi, H.Hussein, L.Gilly

grants access to the supercomputing resources.

Along with Swiss academia, the Federal Government Agencies concerned with national security related to environment benefit significantly from CSCS's service thanks to the ongoing collaboration with MeteoSwiss[8] and the National Centre of Competence in Climate Research for Climatology[9] (NCCR-Climate). In the frame of this cooperation, service reliability and availability of CSCS supercomputing resources provided to MeteoSwiss for the running of their numerical weather prediction operational suite scored over 99% availability over the year.

HPCN Service Highlights

In order to maintain and further develop the high quality of service provided to the broad and heterogeneous national User community, the HPCN Service Division (Fig. 5) has pursued a selected number of projects necessary to the future development of the Service (selected EU and KTI projects including GRID technologies evaluation). The focus of these development projects was twofold: (i) further develop the key HPCN expertise to anticipate future service challenges, and (ii) in-house development of the methodologies and instruments not available on the market (tools for performance, scientific visualization, software engineering for large scientific applications and

[8] http://www.meteoswiss.ch
[9] http://www.nccr-climate.unibe.ch

data basis) in order to provide new added value to users.

HPC Systems Support:

A major success project started in 2003 was the upgrade of the CSCS data Archive facility, which involved both hardware and software upgrades as well as an architectural enhancement to the storage environment, along with the associated migration of the Archive service to the new upgraded environment. The CSCS data management system is designed to accommodate the permanently growing application requirements for total data storage, data movement and total data lifecycle management. The need for a sustainable and scalable annual growth in the range of +50% regarding both the capacity and the access bandwidth implies continuous and balanced extensions and migration towards higher density technology for disk, tape and data access paths, as well as major overall integration.

The aim of the upgrade was to provide users with higher archive access performance and increased service availability, while still ensuring a seamless growth of the archive size. The major interventions and the new components that were integrated within the CSCS Archive production environment include: two new SUN SunFire V880 file and archive servers to increase I/O performance and availability of the file-serving system; Veritas Cluster Software to provide a high-availability solution in case of hardware and software failures as well as to provide absolutely minimum service downtime during periodic maintenance; integration of 6 TB raw of fast Disk Cache based on LSI Logic D280 to increase the cache size and performance, thus keeping a balanced architecture for optimal data moving performance; upgrade to the latest version of the HSM software and Filesystem (SAM-FS/QFS 4.0) to provide enhanced storage management capability and functionality; addition of a FiberChannel switch Brocade SilkWorm 3800 to load balance storage network traffic and eliminate single point of failures within the high-bandwidth FC network that interconnects the file servers with tape drives and disk cache; addition of a stand-by Automated Cartridge System Library Server to ensure redundancy of the tape library control software.

The whole upgrade has been planned to be implemented in steps, in order to minimize the service disturbance to all Users, with interventions scheduled at the times when critical production jobs were not impacted.

HPC Application Support:

In the year 2003 much effort was spent in assisting the scientific community with the multiple facets of software engineering and those of application integration within the CSCS production environment. The aspects ranged from application porting, compilation and debugging, to high level algorithmic optimization, parallelization and vectorization. Solutions were implemented for data management and handling issues. We targeted the optimal integrated use of supercomputers, high speed networks and data management resources. These activities were mainly focused on the IBM MPP achitecture, which was into its first full year of production.

Aiming at an efficient and effective use of the overall HPC facilities, the application support team continued the consolidation and the completion of the Computational Chemistry Framework, as well as the support and maintenance of Mathematical and Numerical Libraries. The available software portfolio now covers a wide spectrum of algorithms and methods, including specific architecture optimized libraries and development tools, along the most widely used Computational (Bio-)Chemistry application suites.

Major achievements have also been made in the support of the NCCR-Climate community[10]. This

[10]NCCR: National Centre of Competence in Climate Research (http://www.nccr-climate.unibe.ch)

community has important requirements not only related to efficient high-end computing, but also to data archiving and pre/post-processing. In this context the local establishment of the climatological ERA40 data base at CSCS represented a first important step towards allowing an integrated and user-friendly access to this data. Currently this dataset is widely used by a number of different research groups at ETH Zürich, MeteoSwiss, POW Davos and the University of Bern.

In parallel we also provided support for the preparation of a new pre/post-processing Linux server that may now be used to access the archived ERA40 data, convert them to the required formats and prepare them for use in atmospheric and climate model simulations. Moreover, several new widely used climate applications where made available on the high-end computational facilities.

The HPC Application Support group has also been involved in the European project PRISM[11], a pilot infrastructure project for the establishment of a EU climate research network. Our primary task was the definition of a set of recommendations and rules defining software engineering processing, coding rules and quality standards. This effort was included within the PRISM System Specification Handbook[12] and proved to be a great opportunity for us to acquire and share new competencies on code portability and code quality standards across multiple platforms. Future involvements in this project will focus on execution performance issues.

Finally, a considerable effort was spent in processing incoming everyday User support requests as well as in consolidating and regularly updating the technical documentation made available under the CSCS User web portal.

HPC Benchmarking and Development:

Major efforts have been invested in the further development of the ”CSCS Performance Environment”, essentially a collection of our own highly specialized system monitoring tools, with a particular focus on sustained performance aspects. Besides others, the performance environment consists on a set of client and server daemons permanently measuring runtime system, jobs and process performance. The currently supported platforms are the NEC SUPER-UX and IBM AIX based systems. Furthermore the server daemons are able to generate very compact process accounting files, that can be easily post-processed by a Java application we developed, reporting detailed accounting statistics at different levels (e.g. process, user, group, institute, application field, ...). Accounting data can be retrieved from databases (Oracle or MySQL) using JDBC API. Unlike other existing products, the tool allows the generation of global system usage statistics, as well as detailed performance analysis of User codes.

The investigation of emerging software technologies (Java, GRID, ..) has also been a key issue in extending the product spectrum that CSCS can offer its users. With the involvement in international projects such as EUROGRID and ENACTS it has been possible to explore GRID technologies. By using the acquired know-how it has been possible to develop a brand new product based on the LM regional weather forecast code able to deliver weather forecasts on demand in a GRID environment.

Advanced Scientific Visualization:

The group provided visualization and media production to the overall CSCS user community and offered advanced prototyping and dedicated support in four activities: To further support our AVS/Express-based Molecular Sciences Visualization toolkit, with greater emphasis for crystallography (cf. Large User Project of Dr. Oganov, ETH-Z); To evaluate, prototype and imple-

[11] PRISM: PRogramme for Integrated earth System Modelling (http://prims.enes.org)
[12] PRISM System Spec. Handbook (http://prism.enes.org/Results/Documents/Handbook/handbook.v.1.0.3.pdf)

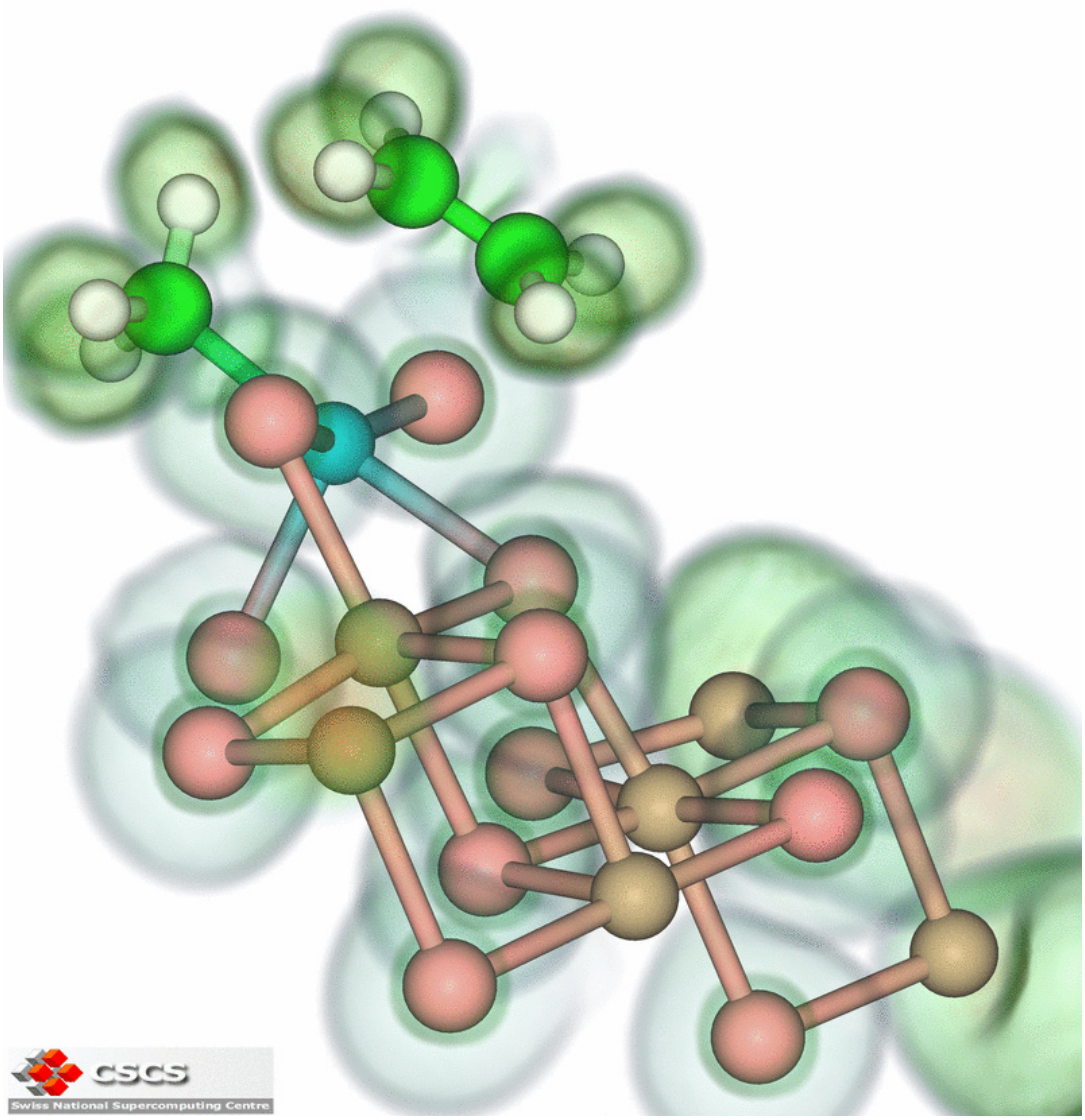


Figure 6: *Data Visualization example: Structure of the pi-complex of an ethylene molecule with a Ti catalytic center in the chemical reaction leading to the formation of polyethylene. A parallel volume rendering of the electronic density around the molecule is performed with the VTK toolkit. A finite difference gradient estimator acts as a volume opacity multiplier to render homogeneous regions almost transparently. Model and Simulation by Mauro Boero (Dept. of Physics, University of Tsukuba) and Michele Parrinello (CSCS), Data visualization by Jean M. Favre (CSCS)*

ment several particle-based techniques for fluid flow visualization (cf. Large User Project of Prof. Kleiser, ETH-Z); to deploy the VTK/ParaView software enviroment on clusters with several interfaces for commercial flow solvers (CFX, TECPLOT, GAMBIT, MemCom) (cf. Institute of the Energy Sciences, EPF-L); and to develop a visualization environment for experimental and numerical data in turbo-machinery flow modelisation (cf. Industrial Project funded by the CTI: ”Anaysis of 3D unsteady free surface flows in Pelton turbines” (see also Fig. 1).

Research Group Parrinello

Modelling the behaviour of condensed systems in physics, chemistry, biology and geophysics has become an essential tool for problem solving. Nonetheless, the gap between what can actually be simulated and the systems of current interest remains very large and needs to be bridged as much as possible. This requires extending the length and time scale of the simulations, as well as their accuracy. To this effect one needs adequate computational resources and algorithms that are able to best exploit the power of supercomputers such as those available at CSCS. In addition new theoretical methods need to be developed as computer power alone is not sufficient.

To this effect my group has introduced a novel method, metadynamics, for extending the very limited time scale of the simulation towards time scales that are more relevant to a large variety of physical and chemical processes. This method has allowed us to explore a large variety of complex processes. Together with the computational muscle of CSCS this has allowed us to solve problems that were previously inaccessible. We are confident that this two-pronged strategy which relies equally on computational power and novel algorithms will lead to further progress in the future.

Michele Parrinello
Departement of Chemistry and Applied Biosciences, ETH Zürich USI Campus

Project title: **Charge Transfer and Oxidative Damage in DNA Fibers**

Project leader: F. Gervasio

Researchers: A. Laio

Institutions: Computational Science, Department of Chemistry and Applied Biosciences, ETH Zürich USI Campus, Lugano

Description

The nature of the electronic structure of DNA has recently attracted great interest due to its potential applications to nanotechnology. Indeed DNA has several properties that make it attractive in a variety of applications. It is a stable polymer and can easily be handled and modified almost at will. Furthermore, its one-dimensional character and regular stacking of pi-bases have suggested the possibility of using DNA as a nanoscale conductor. Unfortunately, experiments have provided very contradictory results. Theory could be of great help in understanding these phenomena provided that all the important constituents of this complex molecule are taken into account (i.e. charged sugar-phosphate backbone, solvating water and counter-ions). Using state of the art ab-initio simulation we investigated a laboratory realizable wet DNA molecule in the radical cation state. We studied the localization of the hole, possible mechanisms of charge transfer and the guanine oxidation. The latter is not only important as a parasite event that stops charge transfer but also from a biological point of view as it represents the first step in DNA oxidation, a common event that in the absence of repairing mechanisms eventually leads to fatal consequences such as cancer and mutagenesis.

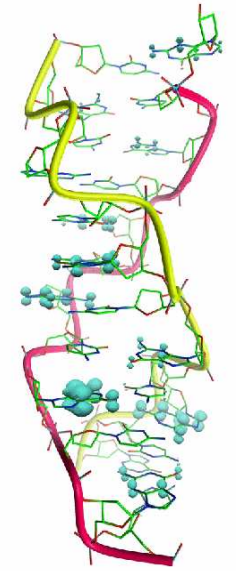


Figure 7: *View of the three-dimensional structure of the G:C decamer and of the spin density isosurface (in cyan) associated to the radical cation state. Water molecules, counter-ions and hydrogens have been removed for clarity. The sugar-phosphate backbone is represented as tubes. Overall the elementary cell contains 654 heavy atoms and 540 hydrogen atoms [the molecular formula is* $C_{228}N_{96}O_{144}P_{24}Na_{24}H_{264} * 138(H_2O)$*]. The isosurface represented has a value of* 10^{-3} *electrons* $Å^{-3}$.

Achievements

We find that at room temperature structural deformation does not provide an efficient localization mechanism. Instead, we find that the the radical defectimportance can be localized by changes in the protonation state.

Moreover we propose a new mechanism for the first steps in DNA radical cation oxidation. The global picture arising from our calculations on the role played by the DNA structure on guanine oxidation is more complicated than previously believed and has even proved surprising in certain aspects. Preliminary calculations performed in gas phase were found to be in excellent agreement with the results found in the literature. These publications predict the pair $G^{\cdot+}:C$ to be more stable than $G(-H)^{\cdot}:C(H)^{+}$. However, when calculations where performed on the hydrated DNA we observed a reversal of the energetic balance in favour of $G(-H)^{\cdot}:C(H)^{+}$ due to the electrostatics of the backbone and the different geometrical structure assumed by the base pair.

We found that the rate limiting step of the formation of 8-OH-G$^{\cdot}$, which is the main product of guanine radical cation oxidation, is the water autoprotolysis. Indeed, once the hydroxide is formed it promptly reacts with the $G^{\cdot+}$. This finding confirms speculations on the importance of DNA structure in changing the products of guanine oxidation. It was suggested that the differences in the products obtained by oxidation of the bases in solution or of the DNA in solution are due to guanine stacking and pairing with cytosine. We found that stacking doesn't play a fundamental role in this case. A fundamental role is instead played by the phosphate backbone, which reduces the barrier for the water protolysis by enhancing the charge transfer from $G^{\cdot}$ to the water and shuttles the lost proton to the water solution. This result confirms previous speculations and could be checked by examining the *G* oxidation in a DNA:PNA duplex in which one strand would be incapable of catalyzing the deprotonation of water, or in a modified DNA were the phosphate backbone is changed into thiophosphate.

Once the 8-OH-G$^{\cdot}$ is formed, the deprotonation of N^1 is impossible since the protonated form is more stable by more than 20 kcal/mol. The overall role of the pairing of guanine with cytosine and the backbone in the oxidation reaction is hence quite subtle: first cytosine takes the proton from guanine radical cation, further stabilizing the radical on the guanine (and localizing it). Once the backbone has catalyzed the hydroxide formation, the pairing favors the 8-OH-G$^{\cdot}$ formation by releasing the proton when needed and greatly stabilizing the product of the reaction. Fluctuations in the structure of the backbone also seem to play a role in aiding proton transfer from one base to the other. Overall we find evidence of a fine-tuned mechanism that acts in double helical DNA to funnel the oxidation reaction toward 8-oxo-G formation.

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Project title: **Using Metadynamics as a Powerful Approach to Docking in Solution**

Project leader: F. Gervasio

Researchers: A. Laio

Institutions: Computational Science, Department of Chemistry and Applied Biosciences, ETH Zürich USI Campus, Lugano

Description

Understanding the mechanism of the recognition process between a ligand and its receptor (docking) presents a fundamental theoretical challenge and has a significant importance in the drug discovery process. The number of algorithms available to assess and rationalize ligand-receptor docking is large and steadily increasing. A distinction can be made between fast and simplified methods and computationally intensive (*accurate*) methods. Methods in the former group are often based on some effective potential that models the ligand-receptor interactions and often assume a rigid receptor and/or ligand. With such methods it is now possible to dock thousands of ligands in a timeline useful to the pharmaceutical industry with varying degrees of success. The second group of methods uses more complex interaction Hamiltonians, flexible ligand and receptors and explicit (or accurate implicit) water solvation and are much more expensive from a computational point of view. Both types of method can contribute to the discovery process: the first group can be used to perform a virtual screening of large libraries while the time consuming methods of the second group are useful in the optimization phase to predict more reliable binding energies and/or to gain a better understanding of the docking process.
The efficiency of the search and optimization methods used to find the global minimum of the ligand-receptor conformation energy is important for the success of both groups of methods.
In our group we recently developed a sampling method (metadynamics) based on non-Markovian molecular dynamics algorithm [1] that proved to be useful in different fields such as in finding global minima for atom clusters, [2] computing the density of states in spin lattice systems [3] and predicting the free energy surface connected to the translocation of an antibiotic through a membrane pore. [4] Given its success in related fields, we think that this method could be valuable in docking since it could be able not only to find the docked geometry and to predict the binding affinity ($\Delta G_{binding}$) but also to explore the whole docking process from the solution to the docking cavity including barriers and intermediate minima. For this reason we tested its performance with respect to the prediction of ligand-receptor docking geometry, of the binding affinity and of the free energy surface (FES) of the whole docking process.

Achievements

This method mimics the real dynamics of a ligand in exiting or entering an enzyme and in doing so reconstructs the FES of the event. We have shown that in the case of the complexes studied the method is able to predict the docked geometry even without any previous knowledge of the structure. In this latter case the metadynamics finds a path leading the ligand from the external solution to the binding cavity. Moreover it quantitatively predicts $\Delta G_{binding}$ the free energy of docking for different ligand/protein complexes and the the $\Delta\Delta G$ of binding of different ligands.
Its added value with respect to many other methods available is that it reconstruts the complete FES including all the relevent minima and the barriers between them. We have shown that this FES is in quantitative agreement to that obtained by running a much longer 2D umbrella sampling. The informations given by the FES could be used to better optimize the binding path and provide a rational to a more powerful computer-aided drug design.

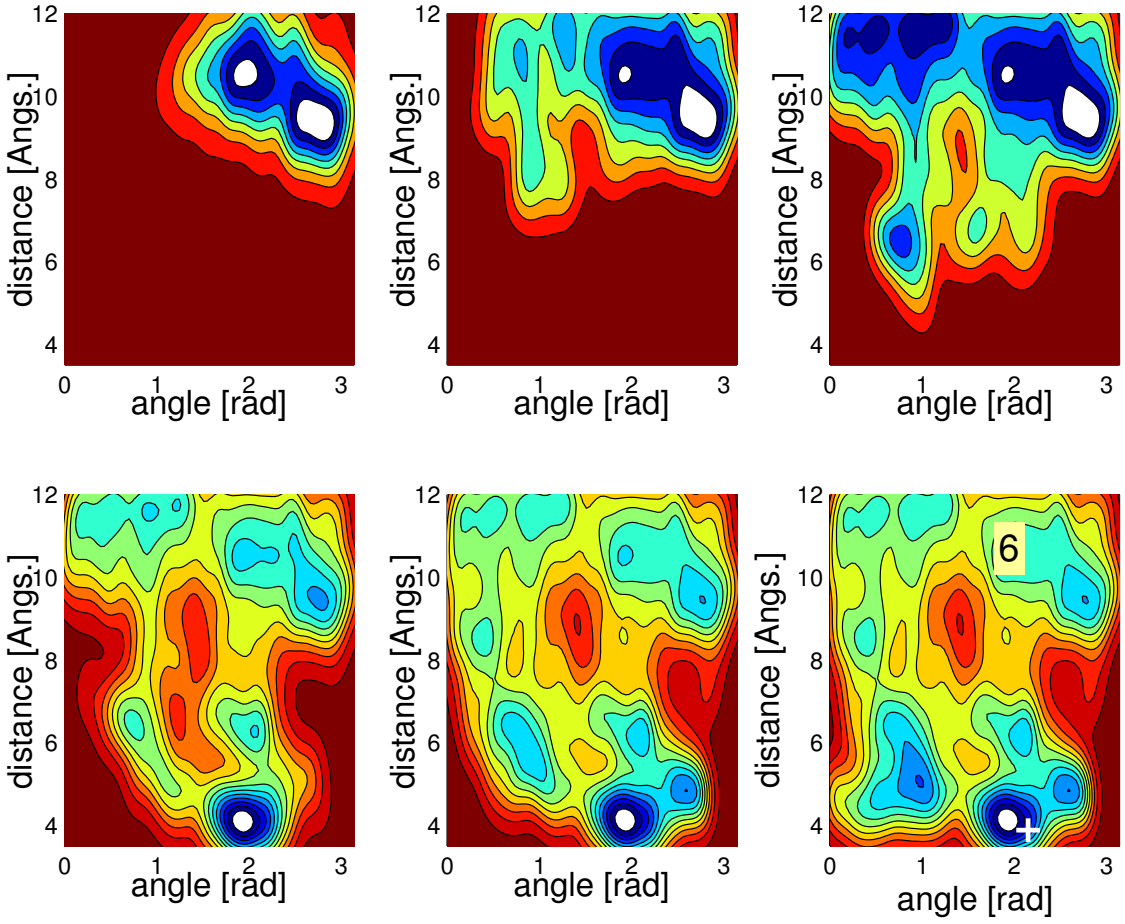

Figure 8: *Free energy surface reconstructed using metadynamics as a function of the angle between the centroid of the enzyme and the atoms C_7 and C_4 of the benzamidine and of the distance between C_7 of the benzamidine and the C_γ of the β-trypsin aspartate 189. The isosurfaces are one per kcal/mol. The total metadynamics trajectory (1000 steps, 3 ns) was divided in six snapshots each adding 166 gaussians to the previous integrated surface to show the dependence of the reconstructed surface on the simulation time. The purple cross in the last snapshot indicates the position of the crystallographic docked geometry.*

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Project title: **Modeling homogeneous catalysis: β–lactone synthesis from epoxide and CO**

Project leader: András Stirling[1]

Researchers: Marcella Iannuzzi[1]
Ferenc Molnar[2]

Institutions: [1] Computational Science, Department of Chemistry and Applied Biosciences, ETH Zürich USI Campus, Lugano
[2] BASF AG, Ludwigshafen, Germany

Description

The formation of β–lactone from epoxyde and CO catalyzed by $CoCO_4^-$ has been studied by a novel *ab initio* molecular dynamics approach[1]. Employing the so–called *metadynamics* methodology, we unraveled the reaction mechanism of catalyzed lactone formation in a fairly unbiased way[2]. First we selected appropriate reaction coordinates and performed the dynamics simulations. Then we identified essential transition and intermediate states displayed by the metadynamics trajectories, which were further refined with static *ab initio* calculations.

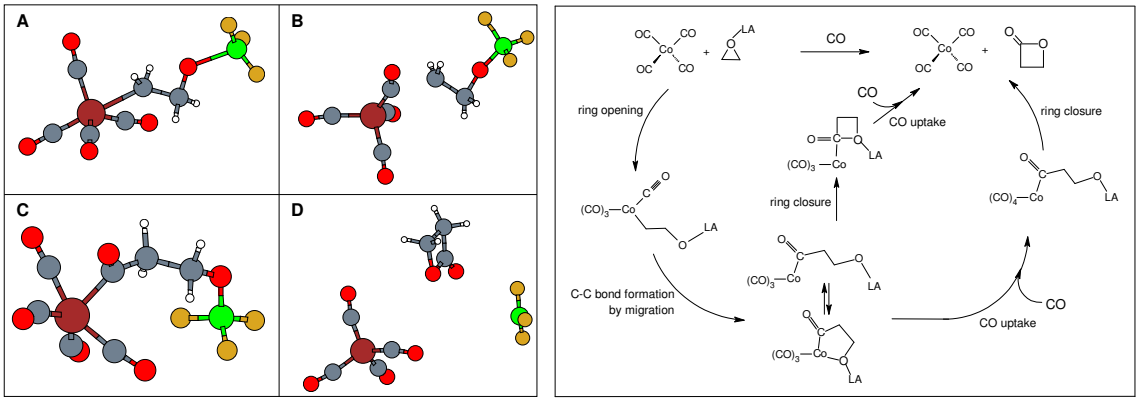

Figure 9: *Left: Snapshots of the most important events of the lactone formation during the typical simulation: A) epoxy–ring opening; B) migration and C–C bond formation; C) by CO uptake, Co becomes 5–coordinated; D) product dissociation and oxygen–Lewis acid bond breaking. Right: Amended reaction scheme. LA indicates Lewis acid.*

Achievements

We were able to reproduce all the elementary steps obtained by previous static calculations. Furthermore we improved the original reaction scheme with additional pathways: we observed an intermediate compound featuring a metalla–oxo–furanyl ring, and described two additional distinct, consecutive reaction steps for the lactone ring formation and the product dissociation.

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MeteoSwiss

During the year under review, MeteoSwiss has carried out all its heavy computations at the CSCS, as it has been doing it for several years. The principal task outsourced to the CSCS is the computation of its numerical model simulating the atmospheric processes over a domain covering most of Western Europe. These simulations, starting from the state of the atmosphere at noon and midnight every day, serve primarily as guidelines for the weather forecasts issued by MeteoSwiss. But it is by far not the sole application. The results of these simulations also serve as input for follow-up models computing air particle trajectories and dispersion of pollutants for the National Emergency Operations Centre (NEOC) located in Zurich as well as hydrological runoff forecasts at the Swiss National Hydrology Survey in Ittigen (BE).

Model results are also sent operationally to the Swiss Federal Institute for Snow and Avalanche Research at Davos where they help to assess the risk of avalanches for the next three days. Next to these governmental institutions, model results are also disseminated to a large number of users like PhD students, researchers, firms and businesses in civil engineering, electricity production, agriculture, etc.

Model development work is done on the computers of the CSCS, too. Model improvement is computationally intensive as any new scheme must be tested with a very large number of different weather situations in order to be certain that it will bring in average an improvement.

As it has already been the case in the past years, the reliability of the CSCS for the production of our weather simulations was in 2003 very high and the support MeteoSwiss received from the CSCS specialists has been irreproachable both for the reaction time in case of problems during the production of the weather forecasts as well as for the improvement of the efficiency of our programme suite.

Modern weather centres are large users of HPC facilities. They need them because their models become, like all the simulation models in science and engineering today, each year more complex, which means more computationally demanding. The supplementary requirement we have in meteorology is that our computations must be performed in a short elapsed time; otherwise their operational utility drops dramatically.

We are pleased to acknowledge that the CSCS has understood the national importance of the simulations of MeteoSwiss in Manno. It has also reacted very constructively and professionally to satisfy the time constrains under which our simulations must take place. For the future, it is for MeteoSwiss of primary importance that the CSCS keeps a very high HPC capability, first of all in computing power, but also in user support, without neglecting the needs for communication and archiving.

Jean Quiby
Head, Modelling Group

Project title: **High-resolution Radar Rainfall Assimilation into the Alpine Model (aLMo) of MeteoSwiss**

Project leader: J. Quiby

Researchers: D. Leuenberger
A. Rossa

Institutions: MeteoSwiss, CH-8044 Zürich

Description

Reliable weather forecasts benefit the public on a broad range of fields and have a high economic value. For instance, some of the more severe weather events can be devastating inflicting loss of life and large property damage in the order of several hundreds of millions of Swiss Francs, consequences that could be mitigated by appropriate forecasts and warnings.

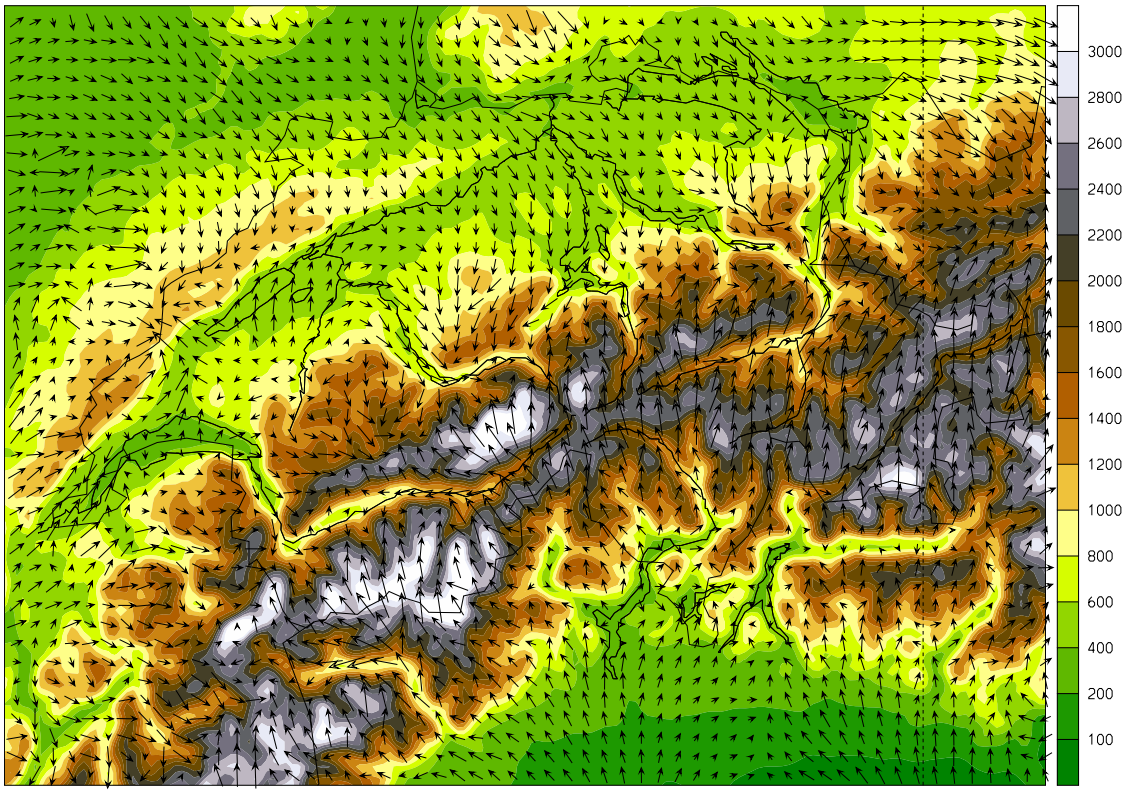

Figure 10: *Representation of the topography (colour shaded) for a high-resolution aLMo simulation (grid spacing of 2.2km). Overlaid arrows show surface winds, whose details forced by topography are often reported as realistic and helpful by MeteoSwiss' bench forecasters.*

Numerical Weather Prediction (NWP) plays an increasingly important role in the operational weather forecasting process. For a region featuring complex terrain, like the Alpine region for instance, a good horizontal and vertical resolution is essential to capture the effects of topography in a realistic manner [1, 2]. For example, the major Alpine valleys along with their tributaries are represented for a mesh size of the order of 1km (Fig. 10), while this kind of detail is virtually absent on a mesh of the order of 10km. Also, it is expected that models with a mesh-size of less

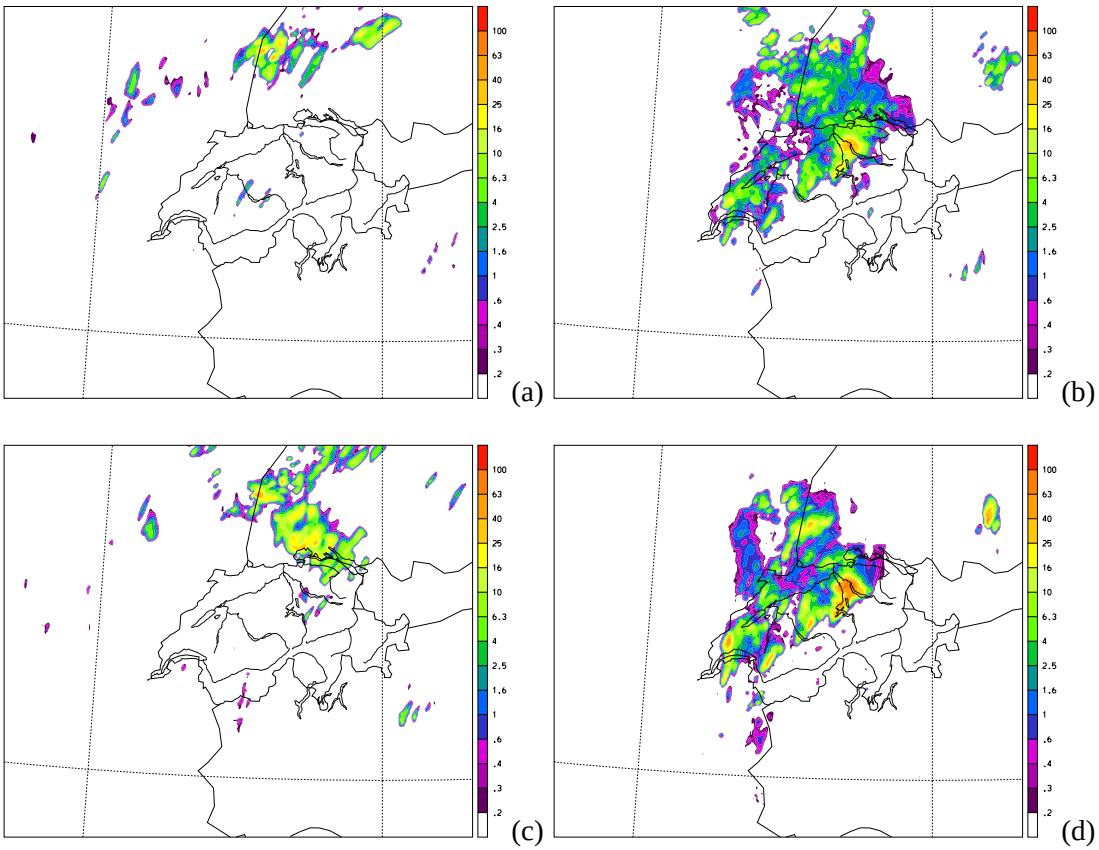

Figure 11: *Hourly sums of precipitation for 8 May 2003 18-19 UTC as observed by radar (panel d) and simulated by the high-resolution aLMo. Panel a) shows the reference run without radar data, panel b) a run with continuous radar forcing and panel c) a run with radar forcing until 16 UTC and 3h free forecast afterwards.*

than a few kilometres can resolve convective precipitation (e.g. thunderstorms) without recurring to simplifying parameterization schemes and thus have a beneficial impact on quantitative precipitation forecasting [10].

An immediate difficulty that arises from NWP models with mesh-sizes of the order of 1km is determining the initial state from which to run a forecast. Conventional observation systems such as radiosonde networks (1 station in Switzerland, some 30 stations in Western Europe) and surface observation (72 automatic stations in Switzerland) are too sparse to capture mesoscale details of a particular weather situation and to constrain the NWP model accordingly.

To tackle this challenge, MeteoSwiss explores the potential of weather radar observations for defining suitable initial conditions. Indeed, weather radars offer high-resolution observations - both in time and space - of precipitation-related phenomena and become more and more important in complementing traditional measurements. This goal is being pursued in the framework of the European COST Action 717 'use of radar observations in hydrological and NWP models' [8], whose 21 participating countries reflect the significant interest in this topic. Weather radar is one important representative out of a number of other remote sensing systems: particularly satellite

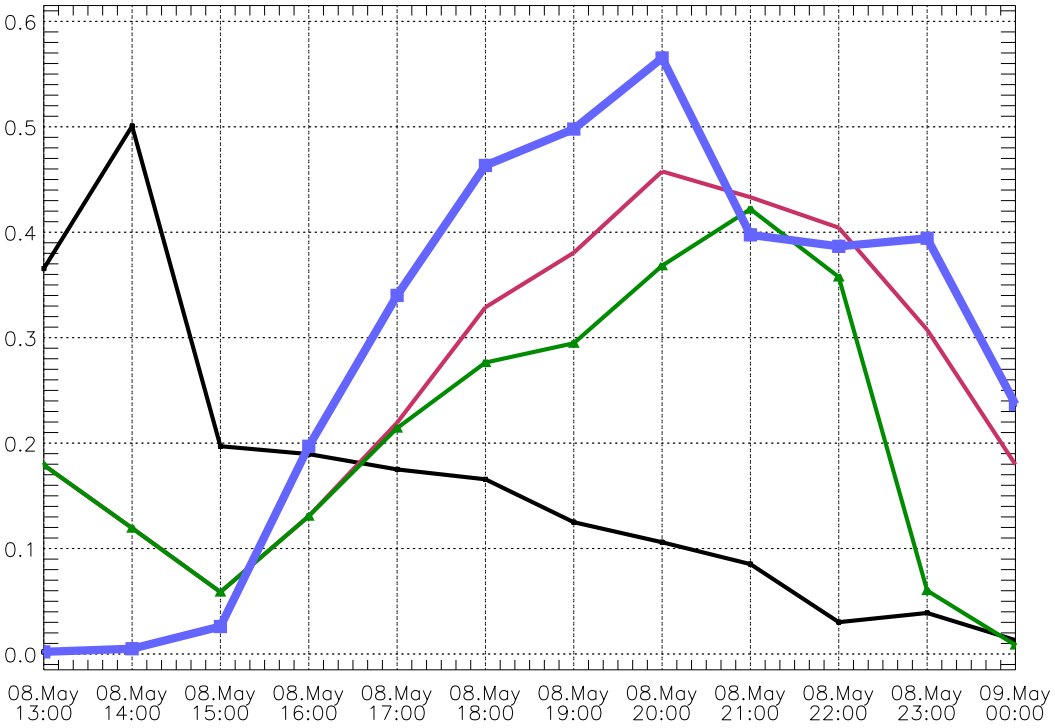

Figure 12: *Domain average of precipitation as observed by radar (blue line) and simulated by the high-resolution aLMo. The black line denotes the run without radar data, red the run with continuous radar forcing and green with radar forcing until 16 UTC and 3h free forecast afterwards. The domain is approximately the one shown in Fig. 11*

based observations as cloud information or GPS derived humidity are currently being explored for assimilation into [4, 5] and verification of NWP models [3, 9, 11].

The method chosen to incorporate the radar information into the NWP model's initial state makes use of the heat released when water vapour is condensed into water droplets nudging the model dynamics towards producing the observed amount of precipitation [6]. This scheme has been adopted for and implemented in the Alpine Model [7] and applied to a case of severe convection over the Swiss Plateau as presented in Fig. 11. Triggered over the central part of the foothill of the Alps the main cell moved to the northeast in a strong south-westerly flow and reached its maximum at about 19 UTC (see radar observation in Fig. 11d). Starting at 8.5.2003 12 UTC and using a mesh size of 2.2km three model simulations were carried out, making more or less use of radar observations. While without radar data the model is not able to capture the storm (Fig. 11a) it reproduces it in very good agreement with the observations when they are continuously included (Fig.11b). Is the insertion of radar data discontinued at 16 UTC and the model run in free forecast mode thereafter a storm results which propagates more rapidly compared to the observed one (Fig.11c). However, at 19 UTC this forecast is clearly superior to the one without radar data, as confirmed by the time evolution of the domain average precipitation shown in Fig. 12 (green versus black line in comparison to the blue line).

With the refinement of the mesh size, the CPU cost of a forecast increases as a power law. Besides the increased number of grid points and the required smaller time step, a refined simulation of the physics (e.g. precipitation, radiation) is also necessary to represent the meteorological phenomena at smaller scale. Although the size of the integration domain can be constrained to reduce the computing cost, one estimates that the introduction of operational forecast at the resolution presented in Fig. 11 will require a ten times increase of available computing power (i.e. about 300GFlops sustained). In order to estimate the confidence of a forecast, many parallel NWP model integrations - an ensemble - could be run from slightly differing initial conditions. Such an approach would claim even higher demands for increased computing resources.

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Large User Projects 2003

At the entrance of CSCS, on the wall, there is a small sentence: *High Performance Computing is an Investment for the Future*. Being so deeply involved on a daily basis with High Performance Computing, this message was so obvious to us that for a long time we thought it was almost a banality. Today we increasingly realize that the real meaning of these few words is not always easy to understand; why should one invest a lot of money in HPC facilities, to often see them outperformed just few years later by departmental servers and high-end workstations ?

We believe that the answer can be found in the next pages. We can only be proud of the quality of the projects and the number of relevant publications that can be related in one way or another to CSCS through computational, data analysis or data visualization services.

Providing adequate HPC solutions to accommodate such a wide spectrum of application requirements is often a real challenging task which can only be achieved through interdisciplinary team work. Coming back to the entrance of CSCS and its sentence, we are currently working hard not only to provide the best match between user and application requirements, technical constraints and the impact on the whole HPC environment. More than ever we are working on understand tomorrow's projects and applications requirements in order to be prepared for the new scientific computational challenges CSCS users will have to face.

Angelo Mangili
Head, HPC Application Support Group

Project title: **Global and regional climate modelling**

Project leader: M. Beniston

Researchers: S. Goyette,
E. Koffi,
B. Koffi,
J.-P. Blanchet†

Institutions: Climate Modeling Group, Department of Geosciences, University of Fribourg
†Université du Québec à Montréal

Description

The NCCR-CLIMATE CESIA project addresses issues of extreme climatic events through regional climate modeling (RCM) approaches; it also addresses the impacts of extremes on forests and mountain vegetation. Currently, three persons are involved in CESIA at the Department of Geosciences of the University of Fribourg, namely Dr. Stéphane Goyette (senior scientist funded by NCCR-Climate, and leader of the regional climate modeling developments), Ms Paula Casals (funded by the Swiss Agency for the Environment, Forests and Landscape, BUWAL, working on the analysis of forest damage and associated hazards such as landslides, following extreme climatic events such as wind-storms), and Prof. M. Beniston (PI of the CESIA project, working part-time as supervisor of the different components of the Fribourg contribution to the NCCR network).

Regional Climate Modeling (RCM) of extreme wind-storms. During the first phase of this project, windstorms (e.g., Vivian) have been simulated with the self-nesting option of the Canadian RCM down to 1 km grid spacing over Western Switzerland. Although the model successfully simulated the hourly mean wind speeds, it failed to reproduce the hourly maximum wind velocities, i.e., the gusts, which in principle exert the most damage on infrastructure and vegetation, in particularly forests. Since late 2002, therefore, significant effort has been undertaken to overcome the problem of underestimation of the simulated maximum wind speed by considering a novel technique, according to the ideas of Brasseur (2001) [4]. The gust parameterization scheme now implemented in the Canadian Regional Climate model allows the simulation of the gusty nature of the wind at the surface and this version of the model has the potential of yielding results on threshold excess that can be of use to other end-users, e.g., specialists concerned with damage functions, or insurance companies. The simulation of windstorms with the newly developed wind gust parameterization has been carried out with success, as reported in the recent paper by Goyette et al. (2003) [5]. This was a necessary step to achieve before considering the development of a ”climatology” of extreme winds in Switzerland for current as well as for future climate conditions.

Experience from the participation of the Fribourg group in the EU ”PRUDENCE” project (5th Framework Program) will be of benefit to the future of CESIA. The self-nesting option of the Canadian RCM for the simulation of specific extreme wind events down to 2 km grid spacing coupled to the wind gust parameterization is currently allowing the development of a numerical high resolution climatology of extreme winds over the Swiss territory. In the framework of the PRUDENCE project, data from the global GCM from the Hadley Centre in the UK (HadAM3H) that has simulated both current climate conditions, i.e., the 1961-1990 period, and a scenario climate (the 2071-2100 period) using the IPCC A2 greenhouse-gas emissions scenario (Nakicenovic et al., 2000) [6], is made available to the other groups of modelers for downscaling studies. The opportunity has thus been seized to make use of these data to drive the Canadian RCM the con-

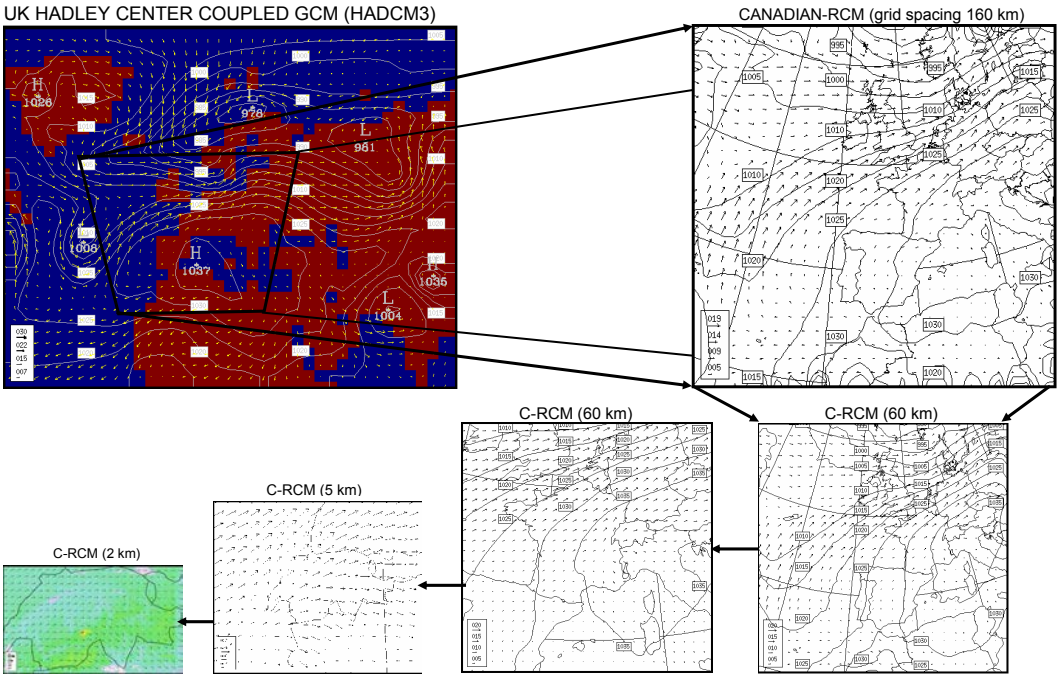

Fig 1. Cascade self-nesting technique used to refine windstorms first simulated with a coarse resolution GCM (here the Hadley Centre's coupled General Circulation Model HADCM3) with the Canadian Regional Climate Model down to 2 km resolution. This technique needs huge computer resources in term of power and memory space.

Figure 13:

text of the CESIA project to simulate the "most extreme" windstorms that occur in Switzerland and surrounding areas during both the reference and future periods. This study will be useful to know more about the behavior of future windstorms in terms of their intensities, their frequency of occurrence, and their locations, on the average. Consequently, it is hoped that the differences between both these climatologies will give information on the change of behavior of extreme these windstorms. Few of these windstorms have already been downscaled at 2 km and their patterns bear a close resemblance to observations, i.e., compared with the 1990 Vivian and the 1999 Lothar storms, as well as a number of secondary but yet severe storms (see Fig. 13). The study of the behavior of these windstorms will thus be of relevance for the economic sector in order to prepare adaptation strategies for a possible increase in the occurrence of these storms.

In parallel, work has been undertaken on the quantification of the behavior of heat waves and their changes in a warmer climate. Results from simulations based on the A2 emissions scenario show a strong warming over much of Europe. The change in mean summer Tmax that intervenes between the reference years 1961-1990 and the future period 2071-2100 generally follows a zonal pattern, implying a northward shift of current climatic zones. A general increase of summer temperatures of about 4 °C is observed primarily because of significant reductions of soil moisture and the consequent positive feedback on lower-tropospheric temperatures. Changes in the 90th quantile of summer maxima (the upper 10% of maximum temperatures) indicate a stronger shift in tempera-

tures for south-western Europe, eastern Europe and on into the Ukraine and Turkey, as well as in the Baltic. The RCM simulations indicate that for many locations an asymmetric shift in extremes occurs as mean summer Tmax increases, i.e., a 4 °C average warming may be accompanied by a 6-8 °C increase in the upper extreme of maximum temperatures. In other parts of the continent, the asymmetry between changes in means and in extremes is much less pronounced, as in the alpine domain north of Italy, for example. The increase in the number of hot days, taking an excess over the 30 °C threshold, is most pronounced in the Mediterranean zone and Eastern Europe, with an additional 60 days or more above 30 °C than under current climatic conditions. In Switzerland, there is likely to be a 5-fold increase in threshold excess by the end of the 21st century, from less than 10 days per year during the reference period, to over 40 days per year in the 2071-2100 period, with absolute annual maxima peaking at 40-45 °C as opposed to 35-38 °C under current climate (with the exception of the very recent 2003 summer heat wave that also affected Switzerland.

Impacts of changing snow conditions on alpine vegetation. In order to illustrate the links between climate simulations and impacts studies, a recent PhD study completed in August, 2003 by Franziska Keller, has shown the value of inter-disciplinary dialog and research in the context of the NCCR-Climate program. In many instances, snow cover and duration are a major controlling factor on a range of environmental systems in mountain regions. When assessing the impacts of climatic change on mountain ecosystems and river basins whose origin lie in the Alps, one of the key controls on such systems will reside in changes in snow amount and duration. At present, regional climate models or statistical downscaling techniques, which are the principal methods applied to the derivation of climatic variables in a future, changing climate, do not provide adequate information at the scales required for investigations in which snow is playing a major role. Using information on climatic change based on RCM simulations, and a snow-depth and energy-balance model developed by the climate research group in Fribourg, Franziska Keller was able to assess the sensitivity of different plants to shifts in the length of the snow-season, i.e., not only in terms of the start of the growing season that is determined by the time of snow-melt in the spring, but also the response of different species to the photo period (day-length that obviously changes if the snow seasons ends 4-6 weeks earlier), and inter-species competition. In addition to the snow-model, studies of the behavior of the snow-pack have been undertaken to support modeling efforts in this study and have been published by Beniston, Keller, and Goyette (2003) [2] and are in press by Beniston, Keller, Koffi, and Goyette (2004) [3].

Vulnerability of Swiss forests to extreme wind storms: current and future situations. A PhD study, financed as third-party funding from the Swiss Agency for the Environment, Forests and Landscapes in Bern, has the aim of assessing the potential for forest damage related to extreme wind storms. A conceptual model relating climate and forests has already been established, in order to identify the different factors that can influence tree mortality in a forest stand, such as windstorms, fire, snow, ice, drought, parasites, and management practices. A spatial database is being set up to incorporate a number of factors that can influence forest vulnerability to climatic extremes, and is composed in a terrain-like fashion using Digital Height Models (DHM), exposure and slope layers, geotechnical data and forest cover data. This data was provided by the GEOSTAT database of the Swiss Federal Statistical Office in Neuchtel. The Swiss Agency for the Environment, Forest and Landscape provided forest damage data following the 1990 Vivian and 1999 Lothar windstorms. First analyses using the new data base have compared the forest damage data of each windstorm in a qualitative manner, with the aim of establishing more quantitative relationships between forest damage and terrain and climatic factors in the near future.

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Project title: **Enantioselective hydrogenation of activated carbonyl compounds over chirally modified platinum**

Project leader: T. Bürgi

Researchers: A. Vargas
A. Urakawa

Institutions: Institute for Chemical and Bioengineering, ETH Zürich

Description

In a combined experimental and theoretical approach we seek to understand heterogeneous enantioselective hydrogenation of activated ketones by modified platinum metal catalysts, which is a promising route for the synthesis of optically pure compounds. A chiral molecule, the modifier, which is firmly anchored to the catalytic surface, is responsible for chiral induction. Much of the experimental effort deals with vibrational spectroscopy with the goal to identify the structure of the active site at the solid-liquid interface of the catalyst. Quantum chemical calculations are used to extract structural information from vibrational spectra of adsorbed and dissolved molecules [1, 2]. Quantum chemical calculations using the ADF program also allow us to study the adsorption of the substrate and modifier on a Pt cluster [3, 4]. Figure 14 shows a calculated structure of a cinchonidine modifier on a Pt cluster, and provides insight into the active site of the heterogeneous catalyst. The main enantiodiscriminating interaction is a hydrogen bond between the protonated quinuclidine N of the modifier and the carbonyl oxygen of the keto group that is hydrogenated [5]. This interaction furthermore accelerates the hydrogenation. Repulsive interactions of the substrate within the chiral pocket likely also play an important role for enantiodiscrimination.

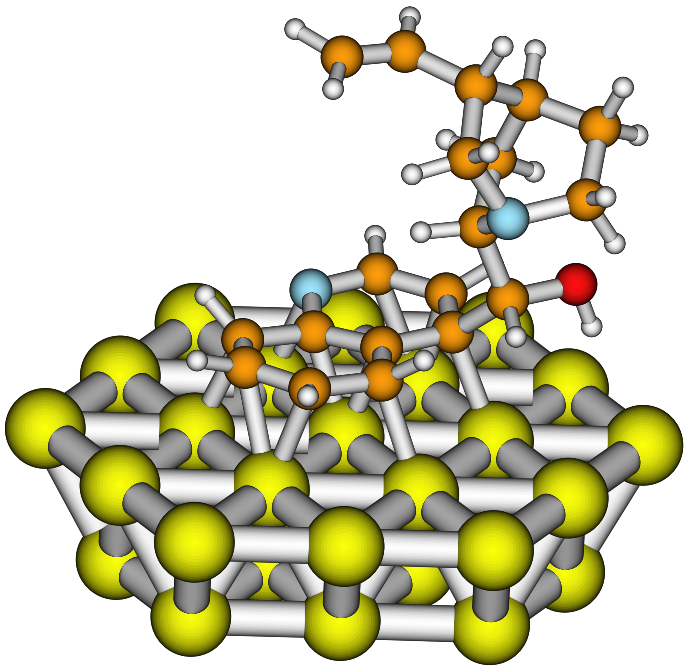

Figure 14: *Adsorption of cinchonidine on a Pt-31 cluster: the formation of a chiral environment close to the surface leads to selective guest-host interactions with the substrates.*

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Project title: **Towards the Development of Reliable Parallel Sparse Matrix Solver Technology**

Project leader: O. Schenk

Researchers: M. Hagemann
J. Mittmann
A. Gupta †

Institutions: Department of Computer Science, University of Basel.
† Mathematical Sciences Department, IBM T.J. Watson Research Center, Yorktown Heights, USA.

Description

We are developing parallel graph-based direct and multilevel iterative algorithms in the broad area of sparse matrix solver technology. Specific topics of research include e.g. algorithms from graph theory such as maximum weighted matchings in bipartite graphs and their application to both parallel direct and iterative multilevel methods. Specific emphasis is placed on applications of algorithms on problems from semiconductor device and circuit simulations, automotive sheet metal forming simulations and nonlinear optimization techniques.

Achievements

During the past few years, algorithmic improvements alone have reduced the time required for the direct solution of nonsymmetric and symmetric indefinite sparse systems of linear equations by several orders of magnitude. In particular, it is demonstrated in [1] that a consistent high level of performance is achieved by the parallel sparse direct solver PARDISO [2]. Experiments show that the algorithmic choices made in the solver enable it to run up to 100 times faster than the best among the other direct solvers for sparse indefinite problems. Thus, the combination of advances in algorithms and a reliable implementation makes it possible to solve such nonsymmetric and symmetric indefinite sparse linear systems quickly and easily, which might have been considered too large for a direct solver until recently. The key features that contribute to its performance include a pre-permutation of rows to place large entries on the diagonal, a symmetric fill-reducing permutation based on the nested dissection ordering algorithm, and a nonsymmetric-pattern factorization that is guided by near- minimal static task- and data-dependency graphs and uses complete nonsymmetric inter-supernode pivoting. A sparse supernode Bunch and Kaufmann pivoting scheme is used for symmetric indefinite systems resulting in an efficient factorization e.g. for saddle point problems. Some of these techniques, such as a right-left looking nonsymmetric pattern algorithm based on static near-minimal DAGs are new, while others have been used in the past, though not as a combination in a single sparse parallel solver.
A major focus has also been the application of the methods to areas from automotive sheet metal forming [3] and semiconductor device simulation, and nonlinear optimization. The solution of these large sparse linear systems is a critical and challenging component and the time for a simulation is often dominated by this part. The sparse solver is expected to balance different and often conflicting requirements. Reliability, a low memory- footprint, and a short solution time are a few of these demands. Currently, no black-box solver exists that can satisfy all criteria. The linear systems from both simulations can be highly ill-conditioned and therefore quite challenging for direct and iterative methods. However, it has been recently shown in [4, 5] that graph-based algorithms - developed to place large entries on the diagonal using nonsymmetric permutations and scalings - also greatly enhance the reliability of both direct and preconditioned iterative solvers for non-

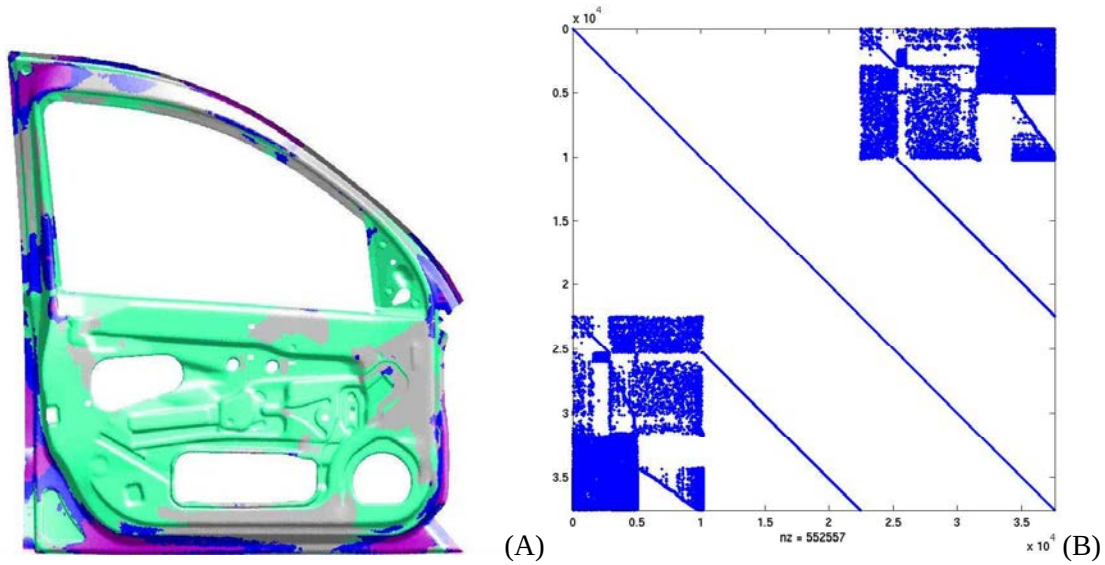

Figure 15: *The figure shows a structure of a symmetric indefinite sparse matrix (A) and the optimization geometry of a finite-element automotive sheet metal forming simulation using Lagrange constraints (B).*

symmetric linear systems arising in semiconductor device and circuit simulations. The numerical experiments indicate that the overall solution strategy is both reliable and very cost effective.
The figure shows a structure of a symmetric indefinite sparse matrix and the optimization geometry of a finite-element automotive sheet metal forming simulation using Lagrange constraints.

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Project title: **Molecular Dynamics Simulations of the Trpcage**

Project leader: A. Caflisch

Researchers: G. Interlandi,
G. Settanni,
A. Caflisch

Institutions: Department of Biochemistry, University of Zürich

Description

Jonathan Neidigh et al [1] have designed a 20-residue mini-protein which folds into a very stable structure. The Trpcage (Fig. 16) (**Asn_1-Leu_2-Tyr_3-Ile_4-Gln_5-TRP_6-Leu_7-Lys_8-Asp_9-Gly_{10}-Gly_{11}-Pro_{12}-Ser_{13}-Ser_{14}-Gly_{15}-Arg_{16}-Pro_{17}-Pro_{18}-Pro_{19}-Ser_{20}**) consists of a α-helix of 7 amino acids followed by a 3_{10}-helix and a short stretch of coil rigidified by three consecutive proline residues. The Trp_6 is en-caged into the hydrophobic core. This peptide is also found to fold very quickly. Qiu et al [2] found experimentally a folding time of 4 μs. In this project we apply molecular dynamics to study its stability at low temperature. The CHARMM forcefield (param22) is used with explicit water and periodic boundary conditions. The waterbox contains $\approx$ 2700 water molecules.

Achievements

Two molecular simulations were started in explicit water at 275K and 300K, respectively. Figure 17 shows the root mean square deviation of the Cα atoms. In both cases the RMSD remains around 2 $\AA$.
A good comparison between simulation and experiment is the number of NOE violations. At 275K the simulation presents 43 NOE violations out of a total of 169 NOEs. Of the 11 NOEs between Trp_6 and the three consecutive Prolines (2 NOE with Pro_{17}, 8 NOEs with Pro_{18} and one with Pro_{19}) 4 are violated within 1 $\AA$ from the upper bound (1 with Pro_{17} and three with Pro_{18}) and one

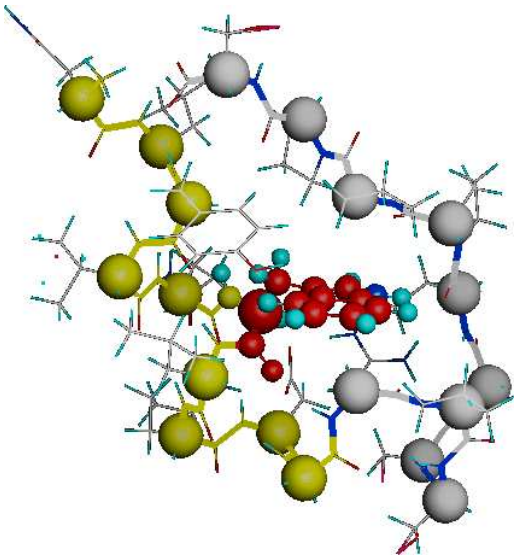

Figure 16: NMR structure of the Trpcage. Trp_6 is in red and the backbone atoms of the α-helix in yellow.

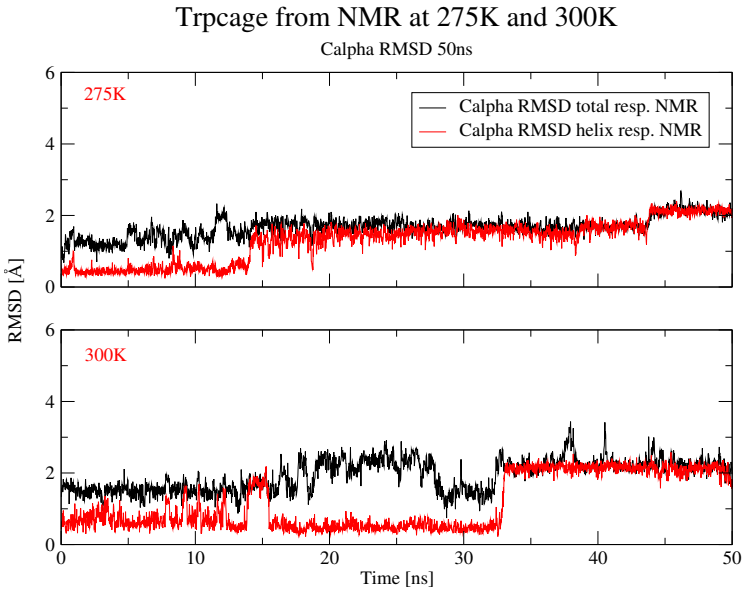

Figure 17: RMSD of the backbone atoms for the simulations at 275K and 300K started from NMR.

is violated within 0.12 $\AA$ from the lower bound (with Pro_{18}). This shows that the NOE measured distances between Trp_6 and the for the stability of the trpcage important prolines are satisfied, or at maximum only weakly violated. Also of interest are the two hydrogen bonds between NH of Gly_{11} and O of Trp_6 as well as $NH^{\varepsilon 1}$ of Trp_6 to O of Arg_{16}. The plot in figure 18 shows the time dependence of the distance between the involved atoms. The two hydrogen bonds are formed only $\sim$ 40 % of the time (by choosing a maximum distance of 2.7 $\AA$). By viewing the snapshots of the simulation with a visualisation tool a very interesting movement of the tryptophan sidechain is observed, where the ring moves back and forth away from Arg_{16}. The distance between $NH^{\varepsilon 1}$ of Trp_6 and O of Arg_{16} has a mean value of 3.2 $\AA$ and, as it can be seen in the plot, reaches in one case a value of above 10 $\AA$ which it keeps for nearly 2 ns. This indicates that the Trpcage is rather flexible even at 275K. Figures 19 and 20 are two snapshots of this molecular dynamics trajectory. The first shows the structure with the tryptophan sidechain in the same position as in the NMR structure and the second the extreme situation where it has rotated away from Arg_{16}.

Conclusions

The Trpcage shows flexibility of the Trp_6 side chain in the folded state. Larger simulations and additional ones at higher temperature are required to observe unfolding and refolding events.

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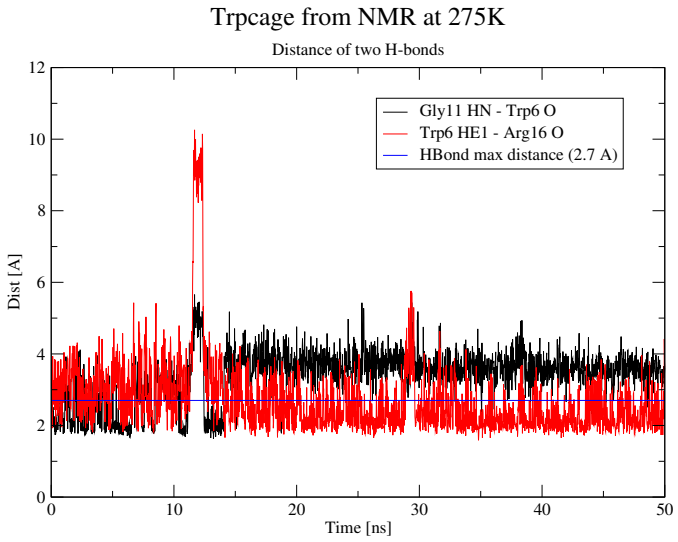

Figure 18: Distance of the atoms involved in the h-bonds from NH of Gly_{11} to O of Trp_6 (black line) and from $NH^{\varepsilon 1}$ of Trp_6 to O of Arg_{16} (red line) as a function of time.

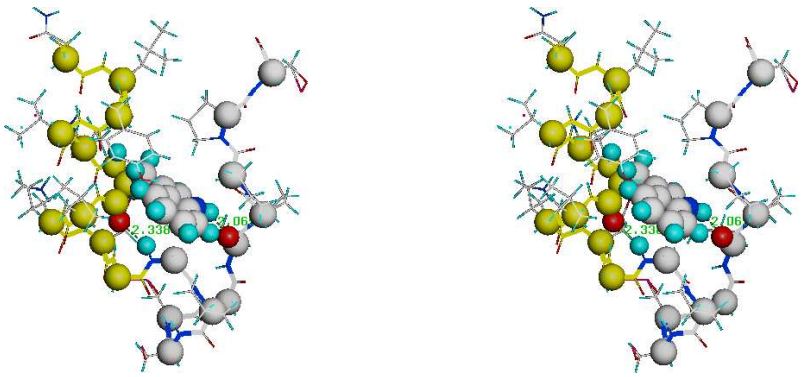

Figure 19: (stereoview) Snapshot of the MD run, where the Tryptophan sidechain is in the correct position with respect to the NMR structure.

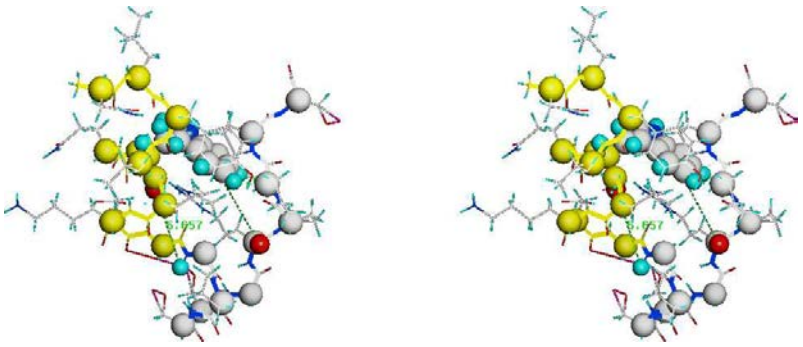

Figure 20: (stereoview) Snapshot of the MD run, where the Tryptophan sidechain has moved away from Arg_{16}.

Project title: **Computation of Stellarator Coils, Equilibrium and Stability**

Project leader: W. A. Cooper[(a)]

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M. Mikhailov[(c)],
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Description

The design of magnetic confinement fusion reactor concepts must satisfy a number of mostly conflicting physics and engineering criteria. Among the physics criteria that must be optimised, we can identify the β limit (β is the ratio of the kinetic pressure to the magnetic pressure of the confining fields) imposed by local and global ideal magnetohydrodynamic (MHD) instabilities [1], the robustness of the magnetic field structure to changes in pressure and current, the confinement of α-particles long enough that they deposit the bulk of their birth energies in the background plasma [2], the confinement of the plasma thermal energy to guarantee sustainability of the burn conditions, etc. Engineering criteria include modularity of the coil system, constraints on coil curvature radii, accessibility of heating and diagnostic systems to the plasma, blanket design conditions to capture and shield the energetic neutrons resulting from the fusion reactions, etc.

The optimisation of the plasma boundary to satisfy the confinement of α-particles, magnetic well in the vacuum configuration and robustness of the magnetic field properties like the rotational transform to changes in β have led to the $\mathscr{J}_{\parallel}$-optimised stellarator configurations. This type of system could hold the potential of stable operation at high β for large aspect ratios and consequently considered for advanced fuel devices with low neutronic load. In more compact stellarators, quasiaxisymmetry offers the potential of good particle confinement because the magnetic field structure is dominantly a two dimensional function in otherwise three dimensional geometric structures. This type of configuration, however, can develop a significant bootstrap current due to the effect of viscous and frictional forces on different classes of particles. The bootstrap current can have an important impact of the equilibrium and stability properties which have to be evaluated under free boundary conditions to assess the full impact. Additional heating is required in a fusion reactor to ignite the plasma, after which the burn should be self sustained. A 3-dimensional global wave propagation code (LEMan; Low frequency ElectroMagnetic code) which includes finite parallel electric field effects (hence electron inertia) has been developed to determine the efficiency

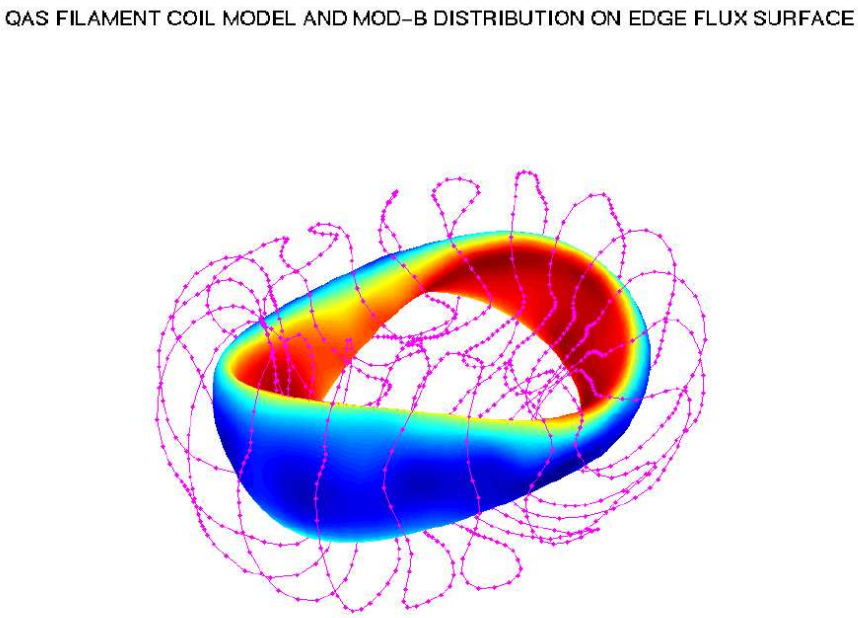

Figure 21: *The coils of a 2 field period quasi-axisymmetric stellarator reactor modelled with filaments, the outermost flux surface computed with the free boundary VMEC code [4] on which the distribution of the modulus of the magnetic field B strength is displayed. The largest values of B are shown in red an the weakest in blue.*

of wave absorption and the power required to heat stellarator plasmas to the high temperatures needed for self sustained fusion [3].

Achievements

$\mathscr{J}_{\|}$ *optimised quasi-isodynamic stellarators with poloidal quasisymmetry.*
Configurations with 6 and 9 field periods have been optimised to have poloidally closed contours of the second adiabatic invariant for deeply, moderately and barely trapped particles, simultaneously. These configurations also satisfy conditions of pseudosymmetry which manifests itself through almost constant mod-B lines closing poloidally, thus satisfying poloidal quasisymmetry. Another important characteristic of these optimised systems is that both the regions of maximum and minimum magnetic field strength B display vanishing magnetic field line curvature. The Pfirsch-Schlüter currents thus localise within one period of the system vanishing around maximum B. The $N = 9$ configuration can achieve stable β values in excess of 10% and further possible improvements could improve its potential as a viable $D - He^3$ reactor. A $N = 3$ configuration with $\beta = 5\%$ that is optimised with respect to quasi-isodynamicity has also been obtained.

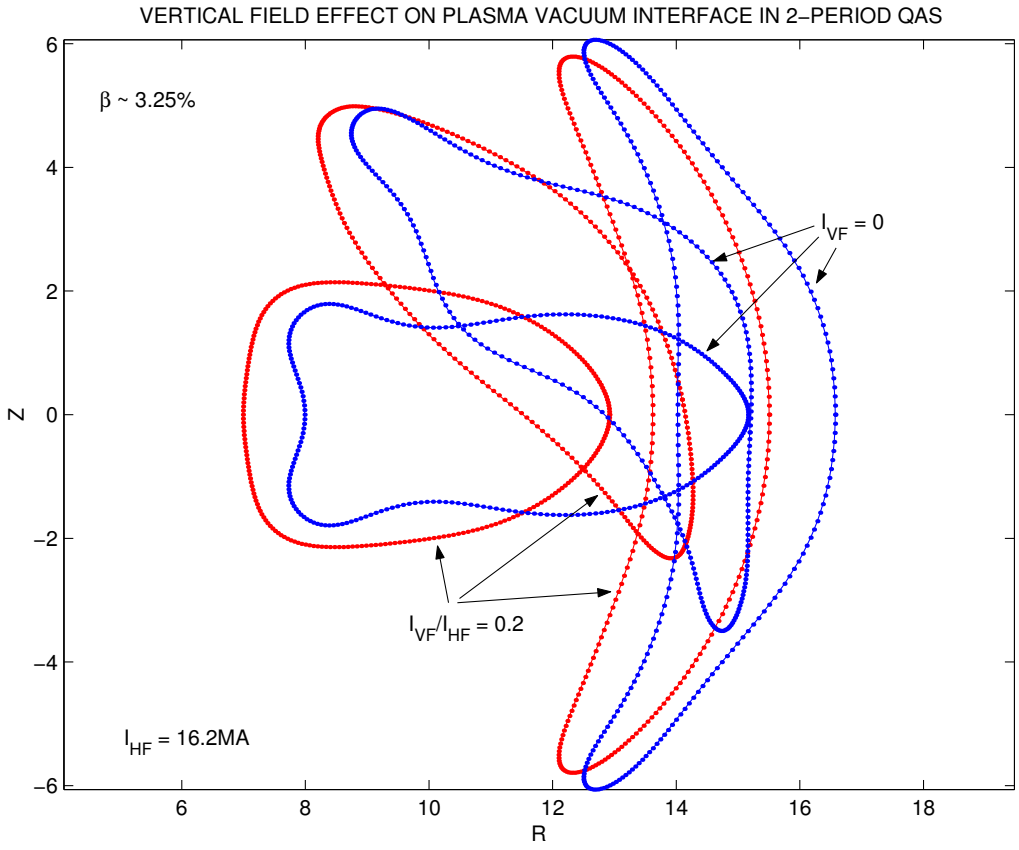

Figure 22: *The plasma-vacuum interface boundary shapes at 3 cross sections within half a field period in a QAS reactor with finite vertical field (red contours) and in the absence of vertical field (blue contours).*

Bootstrap Current Effects on Free Boundary Quasiaxisymmetric Stellarator Equilibrium and Stability.
The impact of a self consistent bootstrap current (BC) in the collisionless $1/\nu$ regime is examined on the equilibrium and global ideal MHD stability properties of a 2-period quasiaxisymmetric stellarator (QAS) reactor under free boundary conditions (Fig. 21). Finite β causes the plasma column to shift outward from the major axis. Adding finite BC causes the column to become more elongated on all cross sections and becomes distorted on the horizontally elongated up-down symmetric cross section. The BC also causes the rotational transform to exceed the critical resonant value $\iota = 1/2$ for $\beta \sim 2\%$ destabilising a $m/n = 2/1$ global external kink. Unlike fixed boundary conditions, the BC fails to converge for $\beta > 4\%$ because not only the current profile varies during the iterations, but the plasma shape changes also. A modest vertical field can restore the vacuum plasma shape at the expense of a mirror term in the magnetic field spectrum (Fig. 22).

Electromagnetic Wave Propagation and Absorption in 3D Plasmas.
The code LEMan [3] has been developed to investigate the global wave propagation and absorption properties in 3D plasma confinement configurations. It solves the Maxwell equations in terms of electromagnetic potentials $(\mathbf{A}, \phi)$ using a finite element discretisation with linear and cubic functions in the radial direction and Fourier decomposition in the angular variables. A comparison

with analytic results in 1D geometry shows that the code recovers the mode spectrum with respect to Alfvén continuum resonance positions, fast magnetosonic wave and global Alfvén eigenmodes. Benchmarking against the 2D LION code shows that the position of the toroidal gap and of the Toroidal Alfvén Eigenmodes are in agreement. Several simplified geometries with selected symmetries (toroidal, mirror, elliptical, helical) have been analysed, all showing the expected behaviour of the modes and gap structures. Two fully 3D geometries have been studied, the QAS and LHD stellarators. In both cases, the spectrum is very complex because of both poloidal and toroidal mode coupling. Still, a comparison with the corresponding cylindrical branches helps to distinguish the main modes and mode conversion surfaces.

Acknowledgments

We would like to thank the support Staff of the Swiss Center for Scientific Computing as well as the on-site NEC application analysts for the kind support provided to this project. This project has been partially sponsored by Euratom, the Fonds National Suisse de la Recherche Scientifique and by the INTAS grant No. 99 – 00592.

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Project title: **ERA40 for NCCR-Climate**

Project leader: H.C. Davies

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Institutions: [1]Institute for Atmospheric and Climate Science ETH Zürich
[2]MeteoSwiss Zürich
[3]University of Mainz

Description

One aim of the National Centre of Competence in Climate Research (NCCR-Climate) is to improve our understanding and modelling skills of natural climate variability and to assess its predictability. Fundamental to this task is a comprehensive climate data base that can be easily accessed in numerical climate model- and analysis-studies. The role of the project ”ERA40 for NCCR-Climate” is to support these research tasks within Work Package II of the NCCR-Climate. It aims to establish and maintain a comprehensive climate database at CSCS where a large part of the numerical studies will be performed as well. The data base covers the last 44 years in 6 hourly intervals and consists of a sub-set of the complete Re-analysis dataset (ERA-40) collected at the European Centre of Medium Range Weather Forecast (ECWMF) in Reading.

The Re-analysis project ERA-40 of ECMWF was a multi-year project funded by the European Union for the establishment of a continuous gridded dataset of the state of the atmosphere. A numerical model based data system was used to create a synthesis of all available atmospheric and oceanic observations (e.g. balloon soundings, satellite and surface station measurements). Numerous meteorological parameters (like temperature, pressure, wind) and derived quantities (e.g. energy fluxes) are thus available globally on a grid with 125 km horizontal resolution and 60 vertical levels.

The establishment of the ERA40 data base at CSCS is also essential for the continuation of other research projects of the involved groups. During the last years, based upon the shorter-period Re-analysis dataset ERA15 (covering the years 1979-1993), a range of investigations has been performed at IACETH to improve our knowledge of various atmospheric phenomena in the most recent decades. Some of these investigations where embedded within international research projects, for instance the systematic Lagrangian study of cross-tropopause transport (EU project STACCATO), and the analysis of Arctic stratospheric temperatures and denitrification (EU project EuroSOLVE). Other analyses focused on short-term climatologies of synoptic storm-tracks, upper-tropospheric jet streams and potential vorticity streamers, and on the importance of large-scale atmospheric transport for the variability of ozone soundings performed by MeteoSwiss at Payerne.

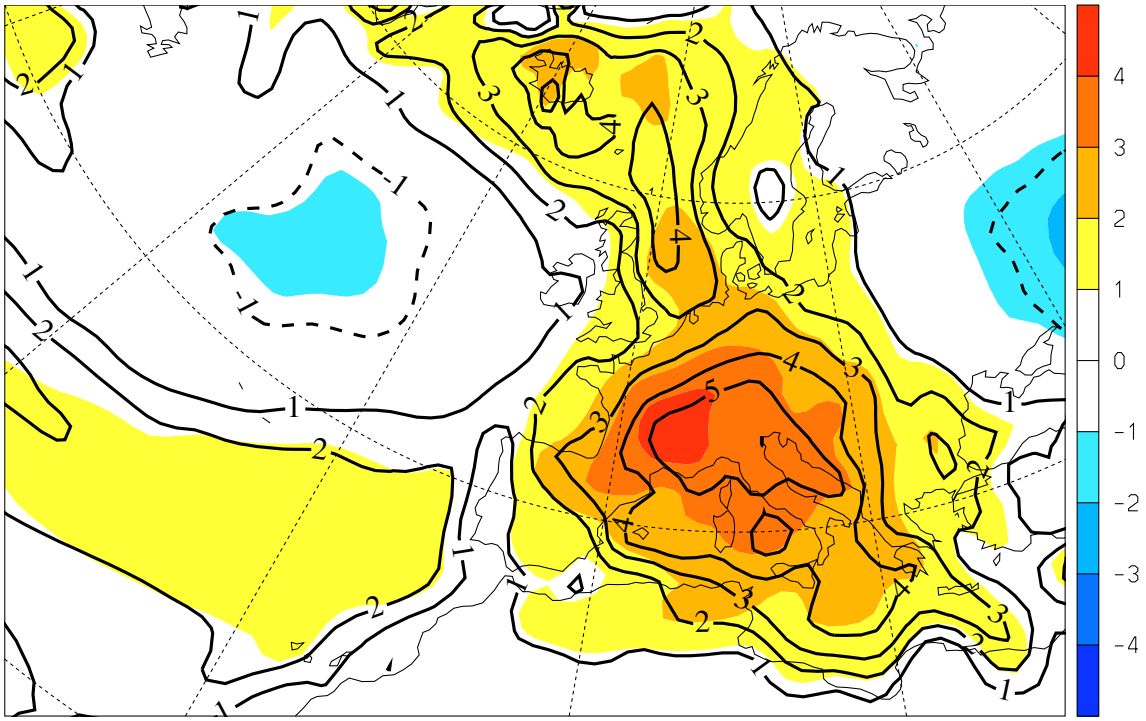

Figure 23: *The JJA temperature anomaly with respect to the 1961-1990 mean for the summer 2003 heatwave. Colour shading show the anomaly in (°C), contour lines display the anomaly normalized by the 30-yr standard deviation (see [1]).*

These studies were only possible due to the availability ofhigh-quality ECMWF Re-analyses from the former ERA15 project. Many of the investigated aspects are likely to be sensitive to climate change (e.g. stratospheric temperatures and denitrification; cross-tropopause transport; baroclinic wave activity) and the establishment of the extended ERA40 data at CSCS permits the investigation of these issues - which are not directly a part of NCCR-Climate, but strongly related to it - for a much longer time period and in greater detail.

The transfer of the raw data had been completed by June 2003 only shortly after the production of the reanalysis data had been finished at the European Centre in Reading. Since then the whole dataset is available to researchers and institutions that have signed an agreement for the use of ECMWF-data with MeteoSwiss. At the end of last year CSCS has installed a new Linux-cluster that serves now as the platform for accessing the archived ERA40 data, convert the data to the required data formats and prepare the data for the use in atmospheric and climate model simulations. Thanks to the excellent support we have received from CSCS staff all the necessary applications could be ported to and installed on the new system in a very short period. The archived data is widely used from a number of different research groups at ETH Zürich, MeteoSwiss, POW Davos and University of Bern.

The ERA40-dataset is also very instrumental for the evaluation of seasonal forecasting systems [2, 3]. While most of the projects are still under way exploring and exploiting this extensive dataset, a few studies have been completed already [4, 5, 6, 7, 8].

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Project title: **Site EffectS assessment using AMbient Excitation**

Project leader: D. Fäh

Researchers: C. Cornou,
I. Oprsal

Institutions: Swiss Seismological Service, ETH Zurich

Description

After recent earthquakes, a priori estimations of site effects became a major challenge for an efficient mitigation of seismic risk. In the case of moderate earthquakes, or moderate motion at some distance from large events, severe damage is often limited to zones of unfavourable geotechnical conditions that give rise to significant site effects.
The numerical prediction of site effects with a reasonable confidence level is usually possible only if geophysical or geotechnical parameters such as the S-wave velocity profile and the geometry of the site are known. The few methods known as reliable appear as far too expensive for local and national authorities, especially in moderate seismicity countries or in developing countries. There is therefore a need for reliable, low cost techniques, from an economical as well as from a safety point of view. Very promising developments were launched over the last decade, based on the use of ambient vibration measurements, which are very easy to obtain in any conditions:

- On the one hand, the H/V technique spread all over the world after Nakamura's paper published in 1989 [Nakamura, 1989]: this technique is claimed to provide the fundamental resonance frequency of the site under investigation;
- On the other hand, in some cases, it is possible to retrieve the P- and S- waves velocity profiles from array measurements of ambient vibrations.

However, one must admit that the physical basis of these two techniques and their actual relevancy for site effect estimates has never reached a scientific overall agreement. Our project at CSCS, performed within the European Commission SESAME project (EVG1-CT-2000-00026), funded by the Swiss Federal Office for Education and Science (BBW Nr.00.0085-2)[13], is thus to thoroughly investigate the capability of these techniques in providing useful, qualitative and/or quantitative information on site conditions and/or site effects through numerical modelling of ambient noise and cross-checking with observed noise.
The numerical codes that have been developed within the SESAME project are used to simulate ambient seismic noise originated by human activity, for sites with homogeneous and heterogeneous subsurface structures. These programs are based on the assumption that noise sources may be approximated by surface or subsurface forces, distributed randomly in space and time.

Achievements

We have simulated ambient noise wave fields for a series of 1D, 2D and 3D canonical models (sedimentary deep and shallow valleys) and some real sites (Grenoble and Colfiorito basins). A parametric study of the synthetic seismic noise time series has allowed deducing the systematic features of the noise and the decisive factors determining resonance frequencies estimated using the H/V technique.
Application of the array processing techniques on simulated ambient noise and cross-comparison with actual noise recordings for real sites was performed in terms of surface waves dispersion

[13] For more information: http://sesame-fp5.obs.ujf-grenoble.fr

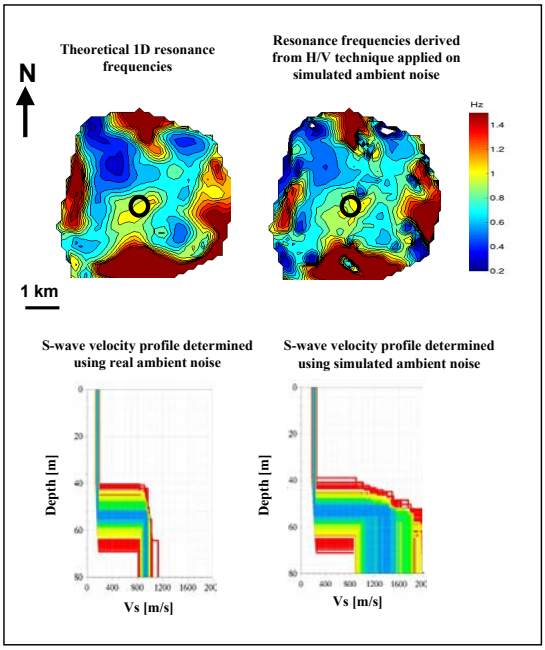

Figure 24: *Simulation of ambient seismic noise for the Colfiorito basin (Italy): (Top left) Theoretical 1D resonance frequencies of the basin; (top right) Resonance frequencies estimated using the H/V technique applied on simulated ambient noise; S-wave velocity profiles derived from actual array noise measurements (bottom left) and simulated ambient noise (bottom right) at the array location indicated by a circle in the top figures.*

curves and inverted seismic velocity profiles. Additional computations for 3D canonical models and real sites are now running and the detailed analysis of noise synthetics for the different models is under progress. Results will be provided by the end of the year 2004.

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Project title: **Computational Science and Engineering in Microelectronics and Optoelectronics**

Project leader: W. Fichtner

Researchers: A. Schenk
A. Witzig
E. Alonso
B. Schmithüsen
S. Röllin
M. Streiff
B. Sahli
S. Brugger
D. Aemmer

Institutions: Integrated Systems Laboratory, ETH Zürich

Description

For the development of novel micro- and opto-electronic processes, devices and circuits, the use of advanced numerical simulation tools has become indispensable. With the continuing advances in semiconductor technology, and the trend to further scaling of the active device dimensions, computational solid state electronics has reached an extremely high level of physical and numerical sophistication. As we are rapidly approaching nanoscale dimensions, effects at the atomistic or quantum-mechanical level are becoming dominant.
We are performing research in a variety of fields in the computational solid state electronics domain. Current projects include the development and utilization of new simulations tools for molecular dynamics studies in material diffusion, novel devices such as single-electron transistors, and optoelectronic devices such as LEDs and laser diodes. For all of our projects, the main emphasis lies in the exploration how accurate physical models can be pragmatically combined with state-of-the-art numerical algorithms. These simulations were carried out on the IBM SP4 system at CSCS Manno and on compute-servers of our laboratory.

Achievements

Efficient and reliable numerical solvers for sparse linear systems and eigenvalue systems are key issues in our research activities in computational science and engineering in microelectronics and optoelectronics. Our simulation problems are 3D, time dependent, highly ill-conditioned and needs locally high resolution. This leads to huge and demanding numerical systems (up to 1,000,000 unknowns), which have to be solved on parallel systems (in the range of 4 to 32 CPUs) with OpenMP and MPI programming techniques. For this reason, a small research group in numerics was established at our laboratory. The scientific goal is development of robust and efficient algorithms on parallel architectures, iterative methods, reduction of CPU time as well as memory consumption. A major result is preconditioner for sparse and highly ill-conditioned linear systems with a remarkable speed-up (e.g. speed-up of 7.4 with 8 CPUs on the IBM SP4 system at CSCS).

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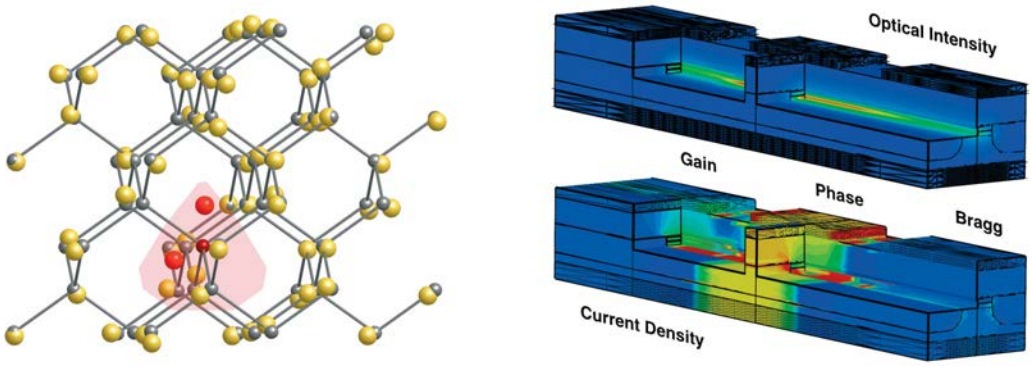

Figure 25: *Ab initio molecular dynamics simulation of dopant diffusion in silicon (left) and coupled electro-optical 3D simulation of a semiconductor laser (right).*

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Project title: **Chiral symmetric Dirac operator in lattice QCD**

Project leader: P. Hasenfratz

Researchers: F. Niedermayer
J. Juge

Institutions: Institute of Theoretical Physics, University of Bern

Description

Quantum Chromodynamics (QCD) is believed to be the microscopic theory describing the strongly interacting particles as protons, neutrons, pions, etc. Apart from an overall scale it contains only a few numbers, the values of the quark masses as input parameters. When the quark masses are set to zero the theory becomes invariant under the so-called chiral symmetry. This symmetry gets explicitly broken by the quark masses in the real world, but still plays an essential role in understanding the low energy properties of strongly interacting particles, the hadrons.

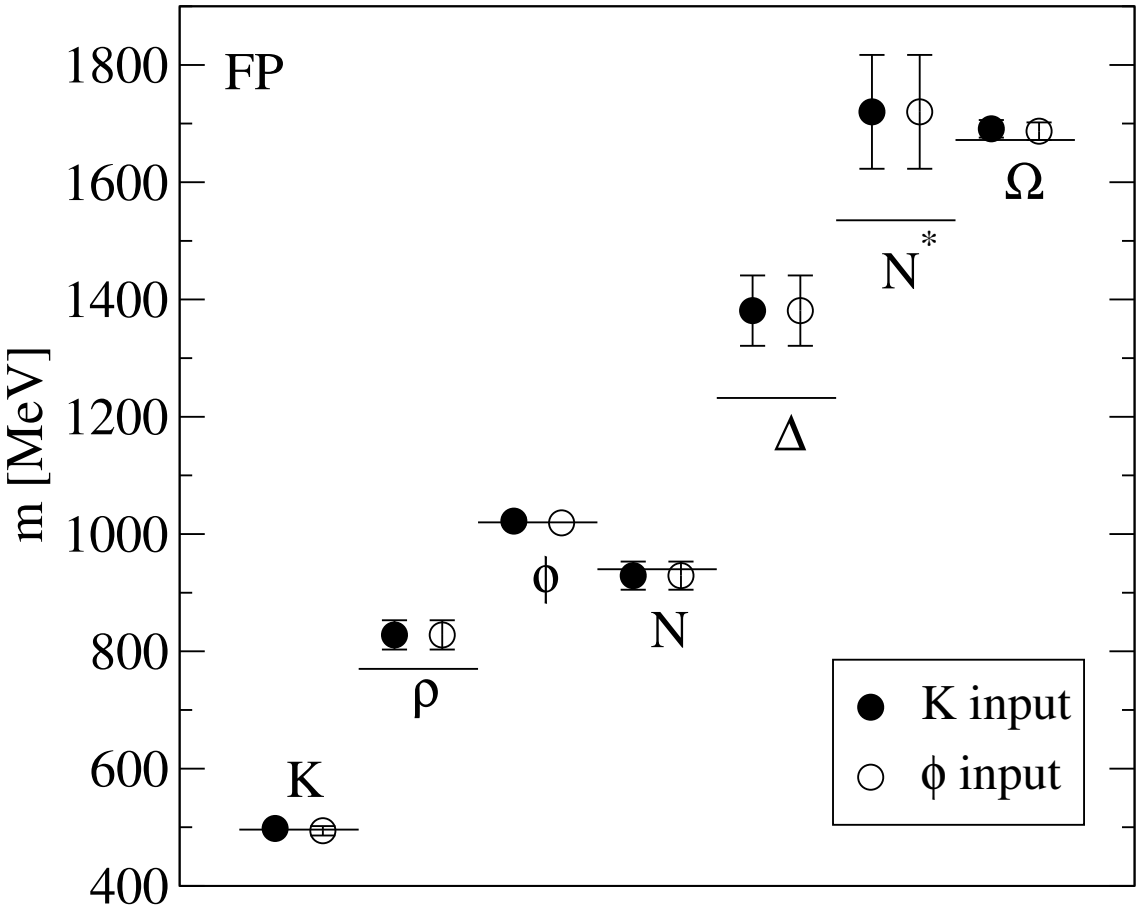

Figure 26: *The hadron masses using the scale parameter obtained from the static QCD potential. The masses of the light and strange quarks are fixed from the observed masses of the* π *and* K *or by the* π *and* Φ *mesons, respectively. The horizontal lines indicate the experimental masses.*

Unfortunately, in the standard formulation of lattice QCD – the discretized version of QCD needed for numerical investigations – the chiral symmetry is badly broken due discretization errors. Recent theoretical developments allowed us to construct a formalism where this symmetry remains intact (for zero quark masses) even at a finite lattice spacing. This makes possible to study the theory at small quark masses and large volumes and perform a safe extrapolation to the physical region.

On the IBM MPP at CSCS and in the framework of the Bern-Graz-Regensburg collaboration on the Hitachi SR8000 in Munich we performed large scale numerical simulations of lattice QCD at different quark masses and volumes, investigating the physical quantities close to the chiral limit. The simulations were performed in the so-called quenched approximation when only the valence quarks are taken into account, i.e. the contribution of the virtual quark-antiquark pairs is neglected. (The simulation of "full" or "unquenched" QCD is more demanding computationally by a factor of ~ 100, and is the aim of the follow-up project.)

Fig. 26 gives our results for a few hadron masses extrapolated to the physical situation, together with the experimental results. It is interesting to observe that the stable/narrow states are described quite well while the broad states (ρ, Δ, N^*) – decaying relatively faster – are off. This is expected intuitively since the neglected quark-antiquark pairs are responsible for these decays.

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Project title: **Photophysics and photochemistry of transition metal compounds: theoretical approaches**

Project leader: A. Hauser

Researchers: L. M. Lawson Daku
A. Vargas
M. Zerara

Institutions: Département de chimie physique, Université de Genève

Description

Photophysical and photochemical properties of transition metal compounds are increasingly being made use of in advanced technological applications. It is thus of more than just academic interest to fully understand the fundamental photophysical and photochemical processes, such as laser-induced luminescence, intersystem crossing, internal conversion, excitation energy transfer or light-induced electron transfer, and the parameters which govern their rates and quantum efficiencies.

Our research interests are focussed on establishing relationships between structural, electronic and energetic parameters, and the dynamics of elementary radiationless processes at a molecular level. Spin-crossover compounds serve as model systems for the investigation of the omnipresent process of intersystem crossing (ISC). Significant progress has been achieved in the understanding of the dynamics of this process using time dependent optical spectroscopy in condensed media at temperatures between 4.2 and 300 K [1].

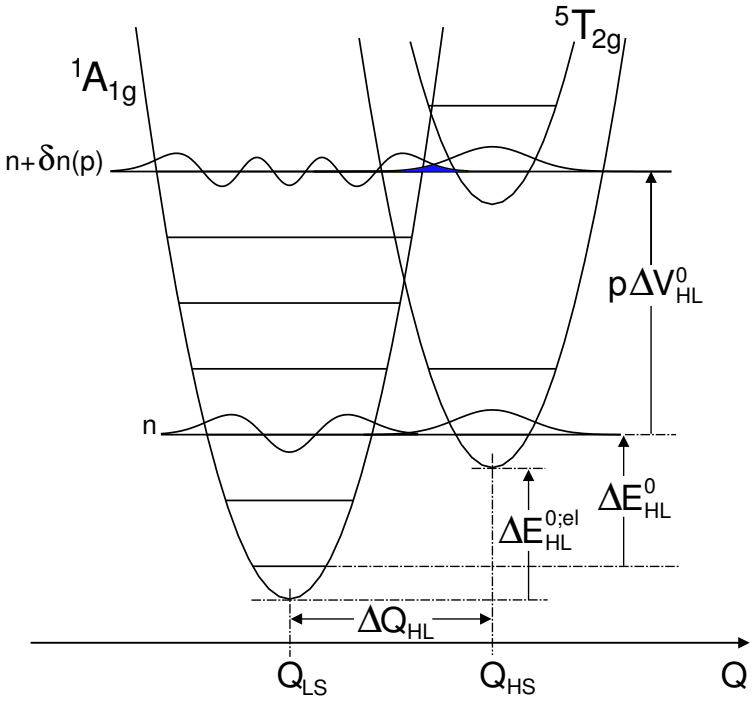
Although the experimental approaches we use are at the forefront of the methods for characterising potential energy surfaces of molecular systems, they characterise the systems mainly around the minima of the surfaces. Furthermore, not all the excited electronic states involved in a photo-induced process are accessible experimentally. Theoretical investigations of the photophysical properties of experimentally studied complexes can be used to overcome these limitations. The large number of atoms in the photophysical systems of interest makes the cost of their study using *ab initio* approaches prohibitive. Hence, one has to rely on approaches based on density functional theory (DFT).

Achievements

During 2003, the resources allocated to our project were principally directed toward the theoretical characterisation of ferrous complexes in the low-spin (LS) $^1A_1(t_{2g}^6)$ and high-spin (HS) $^5T_{2g}(t_{2g}^4e_g^2)$ states, with relation to the thermal spin-crossover and the light-induced spin-state conversion phenomena. This allowed us to achieve significant advances in the understanding of the electronic properties of some comparatively simple transition metal complexes such as $[Fe(OH_2)_6]^{2+}$ and $[Fe(bpy)_3]^{2+}$ (bpy = 2,2'-bipyridine).

The study of the HS $[Fe(OH_2)_6]^{2+}$ complex was motivated by its moderate number of atoms as highly accurate post-Hartree-Fock approaches could be used for its characterisation. The comparison between the *ab initio* LS and HS geometries and the HS-LS zero-point energy (ZPE) difference, on the one hand, and those obtained using different density-functionals, on the other hand, allowed us to assess the performance of the latter ones [2]: it turned out that, while the generalised gradient approximations (GGAs) used give LS and HS geometries similar to the *ab initio* structures, they predict very different ZPE gaps. This makes the energetics the most important property for discriminating between the functionals. In that respect, the best agreement with the best *ab initio* estimate of the ZPE difference was obtained with the RPBE GGA [3].

The LS $[Fe(bpy)_3]^{2+}$ complex, which is larger than the previous one, was characterised using DFT approaches. Indirect experimental information on the excited HS state results from a study of the low-temperature tunnelling in the HS→LS relaxation dynamics which follows the photo-induced population of the HS state (see Figure). By analogy with the Fe(II) spin-crossover complexes for which the metal-ligand bond is shown to undergo the largest structural changes upon the LS↔HS conversion, it is assumed that the reaction coordinate is the totally symmetry breathing mode Q also for $[Fe(bpy)_3]^{2+}$ and that the bond length difference $\Delta r_{HL} = \Delta Q_{HL}/\sqrt{6} \approx 0.2$ Å, too. Based on these assumptions, the relaxation experiments give an estimate for the ZPE difference of $\sim$3500 cm^{-1} for $[Fe(bpy)_3]^{2+}$ doped into the inert host lattice $[Zn(bpy)_3](PF_6)_2$.



Configurational coordinate diagram for an iron(II) complex with a LS ground state along the totally symmetric breathing mode Q. The low-temperature tunneling occurs exclusively from the lowest vibrational level of the HS state. An exerted pressure p adds a work-like contribution $p\Delta V^{\circ}_{HL} = \delta n(p) \times \hbar\omega$ *to* ΔE°_{HL}, ΔV°_{HL} *being the difference in the molecular volumes between the two states.*

Our theoretical study was performed in gas phase, using the same functionals previously employed for $[Fe(OH_2)_6]^{2+}$. It has allowed the validation of the structural assumptions used for the analysis of the low-temperature tunnelling regime. Furthermore, the ability of the different density-functionals to give estimates of the HS-LS energ gap close to the experimental values has been used to further assess the performance of these functionals: for this gas phase study, the RPBE GGA outperforms the other functionals used with a predicted gas phase value for the ZPE difference of 5800 cm^{-1} [4].

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Project title: **CO_2 Trimers**

Project leader: H. Huber

Researchers: I. Boychenko

Institutions: Departement Chemie der Universität Basel

Description

Geometries of five isomers of the CO_2 trimer (see figure 27) were optimized keeping all degrees of freedom flexible. Two of them are known experimentally [1, 2, 3] (**1** and **2** in figure 27) and three others have been found from pairwise-additive ab initio potentials of rigid monomers [4]. We used 3 different ab initio schemes: the standard second-order Moller-Plesset (MP2) method, MP2 with counterpoise corrected gradients by the hierarchical Valiron-Mayer method [5] and the low-order scaling local MP2 theory [6]. Dunning's correlation consistent cc-pV*Z (*=D,T,Q) [7] and aug-cc-pV*Z basis sets [8] were applied with all methods. Resulting optimized geometries and interaction energies have been compared with values obtained previously from several CO_2 dimer potentials to investigate the quality of these potentials. The geometries were also used for subsequent harmonic frequency calculations to get information on local minima and saddle point structures. Counterpoise corrected three-body interaction energies for the CO_2 trimers have been estimated directly from the counterpoise scheme with the MP2 method. All the results from geometry optimization and interaction energy calculations with counterpoise corrections at the MP2 level and geometries obtained from low-order scaling local MP2 method are similar to those obtained with the SAPT pairwise-additive potential at the same level of theory [9].

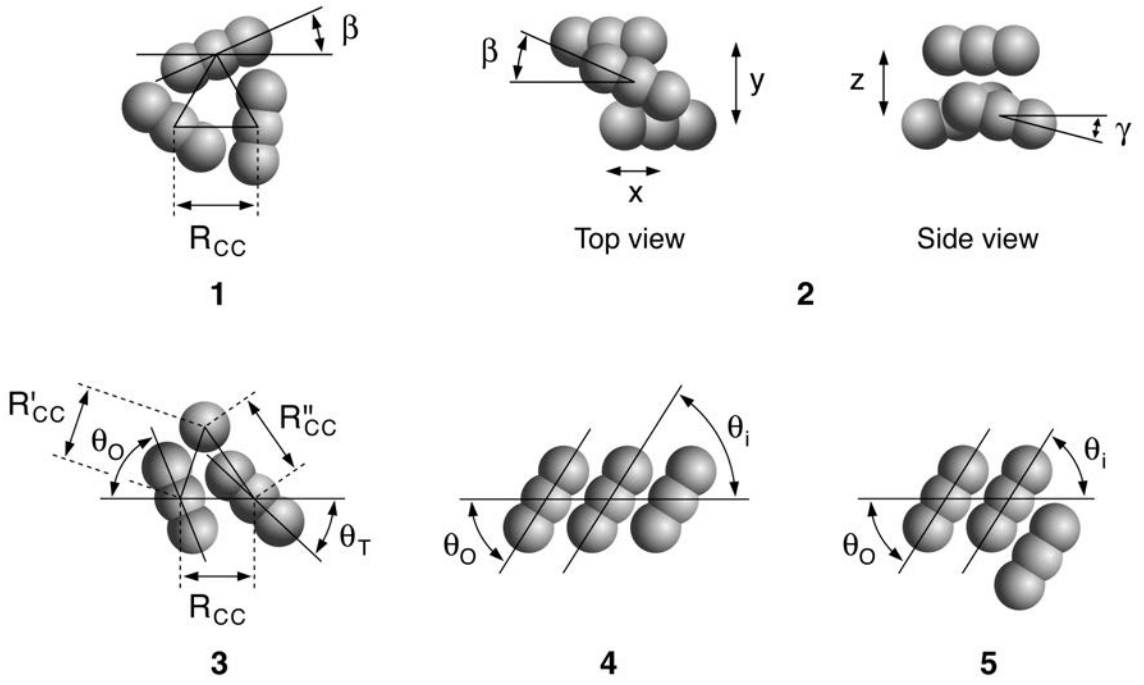

Figure 27: *Five isomers of the CO_2 trimer investigated in this study.*

From MP2/aug-cc-pVDZ counterpoise corrected frequency calculations, three isomers (**1**, **2** and **5**) of the CO_2 trimer were characterized as minima on the potential energy surface and two other (**3** and **4**) were shown to be saddle points. Those CO_2 trimers which are found to be saddle points show repulsive three-body interactions. All the optimization and frequency calculations at the MP2 level were carried out using Gaussian98 [10] or Gaussian03 [11] and all calculations with the local MP2 method were performed with the Molpro2001 [12] quantum chemistry package. Some single point counterpoise corrected energy calculations were performed utilizing a program by P. Salvador [13] that generates necessary input files for Gaussian. The computationally most expensive procedures, counterpoise corrected geometry optimizations with extensive (aug)-cc-pV(T,Q)Z basis sets, had been carried out on the NEC-SX5 supercomputer and would have been impossible without the kind support by CSCS.

Achievements

For five trimers previously found by assuming pair-additivity for rigid monomers and utilizing accurate ab initio potentials, we have shown that two are saddle points (**3** and **4**), when three-body interactions are included. Previously two of the remaining trimers were detected experimentally (**1** and **2**). Experimentalists are now challenged to find isomer **5**.

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Project title: **Development and Application of Time-Dependent Density Functional Theory**

Project leader: J. Hutter

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Description

Photo-induced processes form an important field in chemistry. Every-day examples of light-induced reactions or atomic rearrangements are the photosynthesis and the human vision, the latter resulting from a geometrical change in the rhodopsin due to an electronic excitation. However the description of excitations is more envolved than the determination of the ground state, and thus these methods are still evolving. One quite succesful and computationally feasible method is the time-dependent density functional theory (TDDFT), being similar of fashion and effort as the ground-state density functional theory (DFT). Our goal is to further develop and implement the TDDFT methods in condensed phase environment, allowing us to study excitations in previously unaccessible systems.

Achievements

We have successfully implemented the TDDFT method within the plane-wave basis code CPMD (generally available free of charge at http://www.cpmd.org [1]). This has to be done differently as in the methods based on localised basis sets since the size of the basis is now huge, and this would lead to impossibly large matrix equations if implemented in the same manner. We can also calculate the forces on the ionic coordinates within the Tamm-Dancoff approximation, allowing us to follow the evolution of the system *in* the electronically excited state.
We have verified the implementation and studied the accuracy of the TDDFT method in different small molecules [2]. There we could compare it also to another, more approximative method for the excited states called Restricted Open-shell Kohn-Sham (ROKS) scheme. We found that whereas the accuracy of the two methods was often similar or the TDDFT was closer to the experimental results, there are cases where ROKS leads to a better description. There are also certain, already identified classes of excitations which need in improvement to the exchange-correlation potential (DFT) or kernel (TDDFT) to be able to provide realistic results. We have implemented some new schemes and are presently testing them.
Thanks to the general way the TDDFT implementation [1] was done properties other than the ionic force can be determined *in* the excited state as well. One of them are the density, which is necessary to have an accurate coupling in the mixed quantum mechanical/molecular mechanical (QM/MM) method. This has already lead to first applications in collaboration with the group of Ursula Röthlisberger [3, 4]. We were also involved in the first application of the optical adsorption spectrum of a solvated molecule in a liquid, in the case acetone in water [5]. The optical spectrum requires the determination of the oscillator strength, and for this the dipole moment had to be implemented in the excited state.

A further application of solvation was done in our group. We embedded s-tetrazine (1,2,4,5-tetrazine) in liquid water, and as a reference also calculated the molecule in gas phase and complexes involving one or two water molecules bound to the s-tetrazine molecule. This served as a

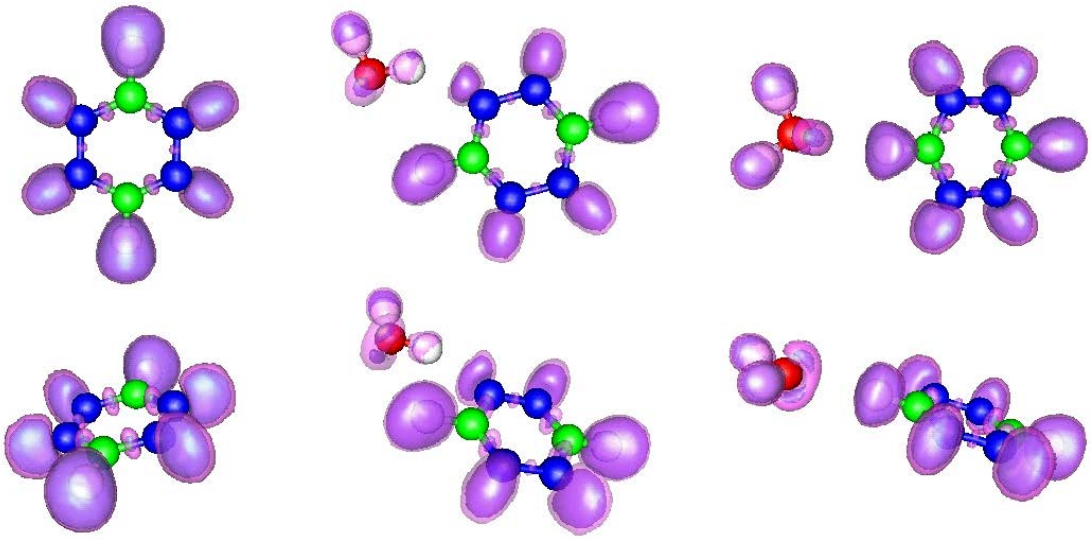

Figure 28: *Isosurfaces of the electron localisation function (ELF) of s-tetrazine (left) and s-tetrazine-1H_2O complex (centre and right). In the first complex the hydrogen bond is formed between the hydrogen of water and one of the nitrogen in s-tetrazine, and in the second complex between a lone pair of the water and the C-H–group of tetrazine.*

way to systematically investigate the interaction of s-tetrazine and water without all the complications from the liquid already.
In Figure 28 we show the Electron Localisation Function (ELF) of s-tetrazine in the gas phase and two different arrangements of a single water molecules acting either as hydrogen bond donor or acceptor. ELF can been seen as a measure of the type of bonding between two constituents, and we can see the difference in the ELF in the two water–s-tetrazine complexes. The water molecule interacting with the nitrogen atom causes a larger change in the ELF than the water hydrogen hydrogen bonded to a C-H–group.
To our suprise we find that the solvated s-tetrazine forms most of the hydrogen bonds to water via the C-H–groups, not with the nitrogen atoms, these appear only in short-lived configurations.
The solvent shifts in the electronic excitations have a different sign for the different excitation energies. We could relate this to the changes of the polarisation of the molecular states of the solute.

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Project title: **Numerical simulation of transitional, turbulent and multiphase flows**

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Description

Most engineering and geophysical flows occur at high Reynolds numbers. Due to their wide range of length and time scales such turbulent flows are not amenable to Direct Numerical Simulations (DNS). In Large-Eddy Simulations (LES), one only resolves the large scales, while their interaction with the non-resolved subgrid scales is modeled. The computational expense thus can be reduced typically by two orders of magnitude. Unlike solutions of the Reynolds-averaged Navier-Stokes equations (RANS), which are the workhorse for present-day industrial flow computations, LES are also able to provide information about the large-scale unsteady flow field that can be crucial for many problems such as fluid-structure interactions or noise generation. In addition, LES can be expected to yield much more reliable results for the mean flow and turbulence statistics than RANS, provided that suitable subgrid-scale models can be found.

The present long-term Project aims at establishing improved techniques for LES that are applicable to increasingly complex transitional and turbulent flows, making use of large-scale computations, including DNS, for the purpose of validation and for the study of phenomena and mechanisms of the flows investigated. For LES we employ the Approximate Deconvolution Model (ADM) which has already been demonstrated to give excellent results for a range of flows including isotropic turbulence, incompressible channel flow, supersonic turbulent boundary layers, compression ramp flow and rectangular jet flow, all at a fraction (order one percent) of the cost that would be needed for a DNS of the same flows.

Aeroacoustic noise prediction tools are still to be developed and are inherently tied to turbulent flow simulations. With an increase in computer power, these simulations for moderate Reynolds numbers come into reach of time-dependent LES. It is therefore strongly desirable to further enhance the understanding of noise generation mechanisms by examining the interconnection between flow features computed by means of LES and the radiated noise.

Particulate flows are an important class of multiphase flows for engineering applications in particular in chemical and process engineering. Within the present project, we investigate the mathematical and physical modeling of dilute particle-laden flows using DNS.

Achievements

1. Large-Eddy Simulation of compressible wall-bounded and massively separated flows

   - Following good results obtained for the turbulent compressible channel flow, the shock -turbulence interaction on a compression ramp was considered in the last LUP period. The presence of a discontinuity in the flow field allowed for testing if ADM, with low-order schemes, can provide a unified modeling of turbulent and nonturbulent (shocks) scales.
     The DNS case of Adams (*J. Fluid Mech.*, 420:47–83, 2000) was selected with a ramp deflection angle of 18°, a free-stream Mach number of 3 and a Reynolds number of $Re_\theta = 1685$ with respect to free-stream quantities and mean momentum thickness at inflow. A fourth-order central spatial discretization was used in conjunction with an explicit four-stage Runge-Kutta temporal integration scheme. No artificial numerical dissipation was used to damp the oscillations developing near the discontinuity, but the order of the secondary filter of ADM had to be adapted locally to the flow physics so as to account for a correct energy dissipation mechanism in the vicinity of shock waves and viscous wall regions. Very good agreement between filtered DNS and LES with ADM was observed with the local adaptation of the deconvolution order to the flow physics.
   - The implementation of the Approximate Deconvolution Model into the semi-industrial Navier-Stokes solver NSMB has been extended for multiblock geometries. The build system of NSMB has been adapted for multiple architectures and compilers. Some simple flow simulations like channel and duct flow at low Reynolds number have been performed during code validation. The pre- and postprocessing has been developed further. Some programming and queueing tools have been created.
     Several type of schemes for the handling of complex geometries with high-order finite-differences have been analysed. The final evaluation of the numerical schemes is in progress.

2. Aeroacoustic computations and large-eddy simulation of jet flows
In this sub-project two different problems are investigated:

   - Computational Aeroacoustics
     In the past period far-field noise was investigated using the established DNS as well as LES data. The previously reported spurious noise which was observed in the LES was further investigated. Spurious waves from the LES data resulted in an unphysical increase of the spectral level at higher frequencies. No improvement could be obtained by evaluating the source terms based on the deconvolved rather than filtered source terms. An analysis of the origin of the spurious contamination of the spectra based on the LES data showed that the main source of errors is due to the acoustic analysis procedure itself. Up to an estimated cutoff frequency the LES reproduces the acoustic results from DNS reasonably well. The analysis confirmed that for the studied flow case LES can be used to predict the dominating part of the acoustic radiation.
   - Large-Eddy Simulation of swirling jet flows
     The main activities in the report period consisted of implementing a proper singularity treatment for cylindrical geometries and to perform validation computations in two

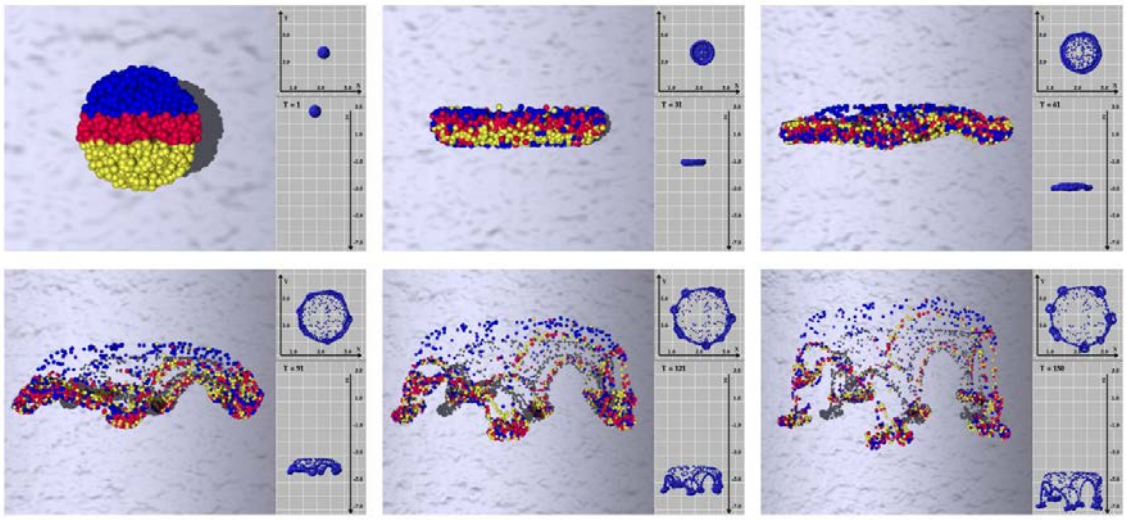

Figure 29: Particle-laden flows occur in many natural processes and industrial applications. A major difficulty is an accurate modeling of the momentum (and energy) exchange between the phases. A suspension drop (cloud of small particles) settling in a fluid under gravity constitutes a simple test case for low Reynolds number flows. At moderate and higher Reynolds numbers interesting phenomena are observed, which are triggered by the particle-fluid interactions.

dimensions. Additional theoretical investigations of forced and decaying isotropic incompressible turbulence focused on the investigation of relaxation regularization as subgrid-scale model and its relation to well-established subgrid-scale model concepts. Furthermore, we analyzed the approximate deconvolution in the nonlinear term with emphasis on the large-scale energetics in isotropic turbulence.

3. Simulation of particulate flows

- Settling and break-up of suspension drops:
  In the previous period the study of suspension drops was continued and extended to moderate drop Reynolds numbers ($1 \leq Re_d \leq 100$). In this range a spherical suspension drop usually deforms into a torus, which eventually becomes unstable and breaks up into a number of secondary blobs. In a systematic way different numerical and physical aspects were examined, such as the influence of the periodic boundaries, the number of particles inside the initial drop, the initial particle positions, and the computational grid resolution. For the visualization of simulation results a close collaboration with CSCS (J. Favre) has been pursued (Figure 29).
- Particle–laden homogeneous, isotropic turbulence:
  Preliminary steps for the simulation of homogeneous turbulence were undertaken, such as the validation of an implemented forcing procedure and the simulation of particle dispersion in slightly turbulent flow.
- Particle–laden flow over a backward–facing step:
  In the previous year models for wall–particle interaction have further been refined. Implementation of the various phenomena like elastic and non–elastic collisions between walls and particles, increased drag coefficient due to the presence of the wall as well as deposition of the particles was completed.

A filter allowing for higher Reynolds numbers calculations was implemented in the spectral–element code. The filter applied is interpolation–based and works by suppressing the unstable mode. More modes can be suppressed on the same basis, if desired, thus constructing a smoother filter. The spectral convergence is not compromised as the interpolation error will go to zero for $N \rightarrow \infty$.

The various forces acting on a particle have been estimated for a range of different flows and aerodynamic types of particles. Following the particle, all known forces were calculated for laminar and turbulent flow in a channel and over a backward–facing step. In addition, the study was conducted also for wall–near regions. For the majority of cases the drag and gravity force terms were found to be by far the most dominant ones, all other forces were significantly smaller. This finding confirms the presumption that a simplified particle force model will be sufficient for larger calculations thereby saving computational time as well as disk space.

4. Large-Eddy Simulation of transitional wall-bounded shear flows

- The analysis of LES models capable of predicting transitional and turbulent incompressible flow in plane channel geometry has been extended. It turned out that for channel flows the usage of the deconvolution operator is not necessary and equally accurate results can be obtained by the use of a relaxation-type model alone. These models turned out to be quite insensitive to the choice of the model coefficient. Moreover, a substantial reduction of aliasing errors could be observed.

  A new class of LES models has been analyzed with the introduction of high-pass filtered eddy-viscosity models, e.g. the high-pass filtered Smagorinsky model and the high-pass filtered structure-function model. The introduction of the filter operation allows to perform simulations of transitional flows even without the use of dynamic modeling.

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Project title (1): **Multi-scale Simulations using Particle Methods: Towards the development of multiscale computations for biosensors**

Project title (2): **Machine learning algorithms and applications**

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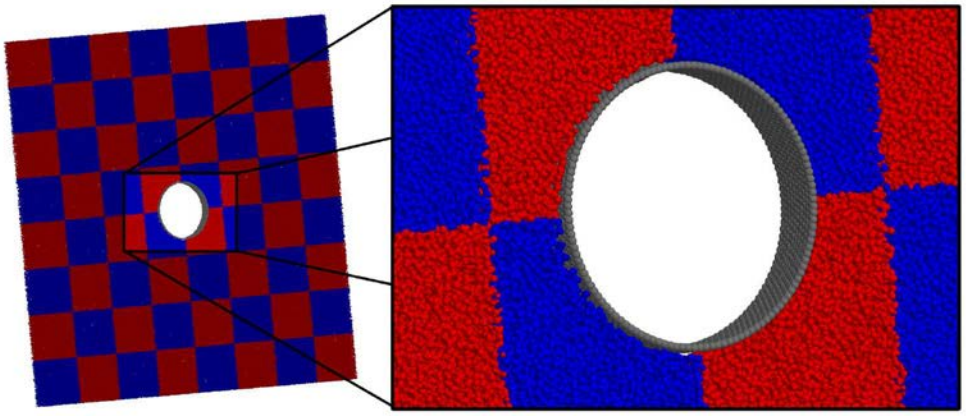
Abstract (1)

We are developing particle methods, such as vortex methods, smooth particle hydrodynamics (SPH), and molecular dynamics (MD), for the simulation of flows in the continuum and the nanoscale level. Our current emphasis is on particle methods capable of bridging multiple length and time scales.

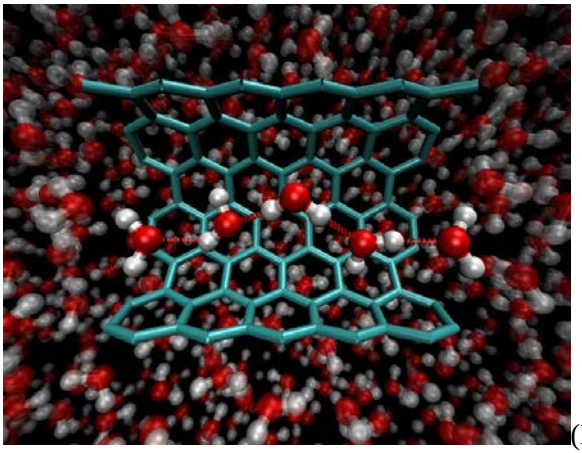
The studies involve MD simulations various forms of carbon in aqueous solutions e.g., water droplets on a graphite surface and carbon nanotubes in water [1, 2, 3, 4, 5, 6, 7]. Figure 30(A) shows the parallel decomposition of a one-million atoms simulation for the study of water flowing past a carbon nanotube. In other simulations we study the filling and emptying of narrow carbon nanotubes cf. Figure 30(B). The interaction potentials used in these MD simulations are calibrated by considering the experimental macro-scopic contact angle of a water droplet on pristine and doped graphite surfaces cf. Figure 30(C) [2, 5]. We are furthermore performing quantum chemistry and density functional theory calculations in collaboration with Dr. Richard Jaffe at NASA Ames Research Center and with Prof. Parrinello at CSCS to derive potentials for water-graphite systems cf. [8, 9, 9].

In the field of material science, we consider the structure of silica nanoparticles in collaboration with group of Prof. Pratsinis, ETH and the melting of nobel metals inside carbon nanotubes with the group of Prof. Poulikakos, ETH.

To reach length scales not accessible through direct molecular dynamics simulations, we employ multiscale techniques and couple the molecular system to continuum Navier-Stokes models [10, 11] cf. Figure 30(D).



(A)



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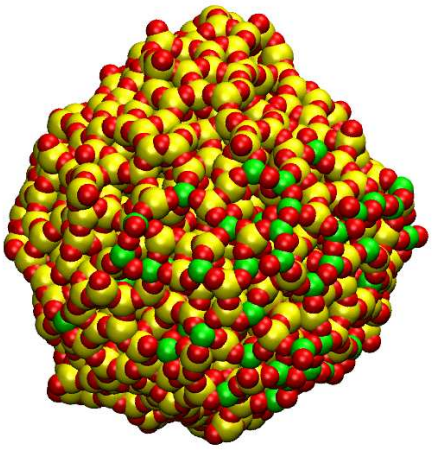

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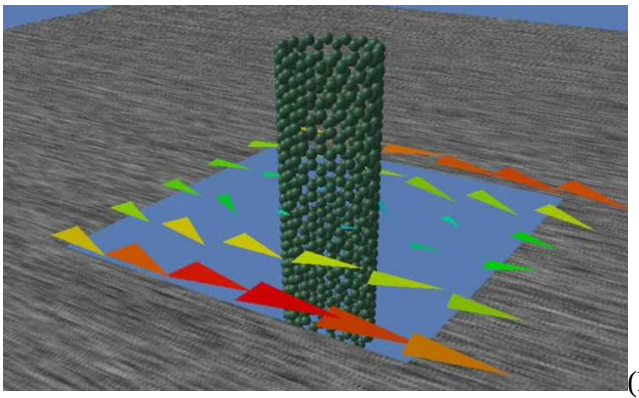
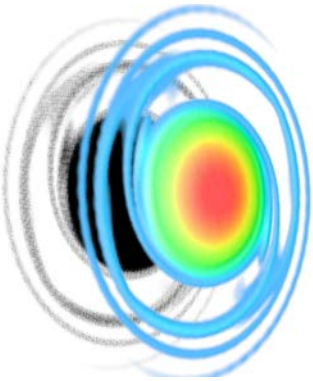


(D)



(E)

Figure 30: *The pictures show (A) the parallel decomposition of a one-million atoms MD simulation of water flowing past a carbon nanotube. water, (B) the filling and emptying of a narrow carbon nanotube, (C) the structure of a* SiO_2-TiO_2 *nanoparticle, (D) simulation of flow past very large nanotubes using multiscaling techniques. We finally consider adaptive vortex methods employing a variable particle size to resolve the small scale structures in boundary layers (E).*

Our macro-scale studies include smooth particle hydrodynamics method for the simulation of fluid-structure interaction in soft tissue [12], and adaptive particle vortex methods in fluid dynamics (Figure 30(E)).

Abstract (2)

We are developing biologically inspired optimization algorithms and apply them to challenging real-world problems that cannot be solved by classical optimization methods. Specific topics of research include the further enhancement of existing bioinspired optimization techniques and their application.

Learning Distributions and Surrogates in Evolutionary Algorithms We analyse and (empirically) compare different continuous domain evolutionary algorithms that learn probability distributions from their sample populations [13] or use a surrogate fitness function [14, 15]. The exploitation of the information contained in candidate solutions evaluated in the past is a key feature with regard to the performance of an optimization algorithm. Algorithms usually differ in the type and amount of past information they utilize. One can distinguish between algorithms that solely use parameter values and rank information of past candidate solutions, and algorithms that additionally use the computed values of the costfunction (e.g. surrogate methods). In the former algorithms, one of the key concepts involves the identification of correlations between parameters of selected individuals and the use of these correlations to accelerate the convergence rate of the algorithms. In the latter case, a particulary promising approach is the use of Gaussian process regression, as it provides the key advantage of predicting an uncertainty measure in the form of a standard deviation for the predicted function value. Empirical studies on a set of 15 test functions are conducted. In low dimensions, the surrogate method clearly outperforms other approaches. For higher dimensions building a reliable surrogate becomes increasingly difficult and efficient distribution estimation becomes superior.

Control of Thermoacoustic Instabilities Thermoacoustic instabilities are a phenomenon occuring in lean premixed low emission gas turbines, jet engines, afterburners and liquid-fuelled rocket motors. They cause unsteady heat release and pressure oscillations and lead to excessive vibrations resulting in mechanical failure, high levels of acoustic noise, high burn rates, and possible component melting. The objective here is to achieve a control strategy for a large-scale stationary gas turbine. For this end a physically based model is developed. Parameters of the model are estimated from measured data. This estimation problem is characterized by (a) parameters that are changing in time and (b) high noise levels that need to be covered. Based on recent improvements of the CMA evolution strategy [16, 17] we develop a new technique to cover both problems at the same time. The idea is to implicitly detect weak signals and increase the respective search distribution variance in this case. The technique does not incorporate problem specific knowlege into the algorithm. Experiments are performed to identify reasonable strategy parameters in this concept. The application of the developed algorithm to the primary identification problem is ongoing work.

Bayesian Optimization Algorithm Applied to Spin Glasses The task of finding ground states of spin-glass systems is a well known problem of statistical physics. We consider a special case, where the spins are arranged on a two- or three-dimensional grid and each spin interacts with its nearest neighbors only. Spin glass instances with discrete coupling and with normally distributed coupling constants are used. We investigate the usage of a mixed Bayesian optimization algorithm (MBOA) [18] for solving spin glass instances. MBOA

combines techniques and concepts from genetic and evolutionary computation, machine learning, and statistics. The parallel Mixed Bayesian Optimization Algorithm is able to utilize a cluster of workstations to perform the construction of Bayesian network in parallel. The performance is improved by combining MBOA with a local searcher, the discrete hill climber (DHC). DHC decreases the required number of evaluations approximately tenfold. To estimate the scalability of MBOA on 2D Ising spin-glass systems, we tested them on random instances for problems ranging from 6×6 to 20×20 spins, 1000 random instances for each problem size. The results indicate that MBOA performs similarly as the best problem-specific approach; the time complexity can be estimated as $O(n^{3.5})$ [19]. Currently, we perform experiments to estimate the scalability of MBOA for 3D Ising spin glass systems.

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Project title: **Direct Numerical Simulation of the Buoyancy-Driven Turbulence in a Cavity: the DNSBDTC project**

Project leader: E. Leriche

Researchers: E. Leriche

Institutions: LIN-ISE-SGM, Ecole Polytechnique Fédérale de Lausanne, CH

Description

When a fluid enclosed in a cavity is heated over one vertical wall and cooled over its opposite at equal rates –all other walls being adiabatic–, a complex flow develops. The flow characteristics depend on the non-dimensional system parameter known as the Rayleigh (Ra) and Prandtl (Pr) numbers. This problem is one of the classical heat and mass transfer problems with significance for fundamental fluid mechanics, as well as for engineering –the cavity domain is a good approximation to the geometries commonly found in practice– and geophysical applications, like for instance, industrial cooling systems, crystal growth procedures, building insulation or buoyancy-induced horizontal mass transfer in geophysical flows.

Estimates for the attainable turbulent Reynolds/Rayleigh number by the method of direct numerical simulation have been known for several decades. The evolution in computer hardware and algorithmic developments make it now possible to extend this technique to transitional turbulent flows that are inhomogeneous in all space directions. At present, this is at the limit of what can be achieved with confidence. The present project is concerned with the numerical and physical aspects of the direct simulation of incompressible turbulence within a side-heated cubical cavity. The goal of this project is to reach the highest Rayleigh number but in a very simple domain, a cubical cavity. This simple geometry leads to a very efficient code.

The flow phenomena encountered within such systems are many and poorly understood. At sufficiently high Ra numbers the ascending layer which develops on the heated side undergoes transition to turbulence. A corresponding flow pattern develops on the cooled wall where a descending layer also undergoes transition. The action of these two streams combine to generate a global circulation pattern that sets up a positive vertical temperature gradient over the central part of the cavity which tends to suppress turbulence. As a result some of the turbulent energy generated near the walls is used into setting up a set of internal gravity waves. Another strange phenomenon that is sometimes found in turbulent buoyant flows under density stratification is that of counter-gradient heat transfer (the mean flux of heat due to the turbulent fluctuations is against the mean temperature gradient.) This has been studied in the context of homogeneous flows but not within a complex flow domain.

The scientific aims are the study of the transition process by buoyancy forcing, the enhanced heat transfer due to the development of turbulence, the collapse of the turbulence under stable stratification conditions, the role of the gravity waves in the global circulation and, if possible, the heat transfer scaling laws.

The objective is to study in detail the three-dimensional turbulent and laminar flow properties within a side-heated cubical cavity by means of direct simulation at high Rayleigh numbers : between 10^5 and 10^9. The simulation will be based on the numerical solution of the Navier-Stokes equations with a Boussinesq buoyancy forcing by spectral methods. The resolution to be used, at least 3.0 million modes, will enable the detail representation of all dynamically significant scales of motion. To our knowledge, such detailed study of this type of complexity is not available from the scientific literature.

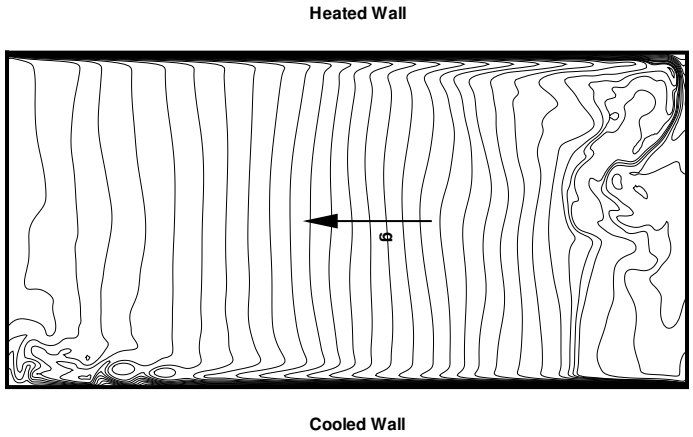

Figure 31: *Instantaneous temperature contours in a side-heated cavity.* $Ra=3\times10^8$. *3D DNS using Fourier-spectral element approximations.*

Achievements

1. A recent numerical study of natural convection in a side heated cavity has been carried out. The geometry is that of an 'open' cavity meaning that the domain in the direction parallel to the heated walls but normal to the gravity vector is infinite. The usual approximation of such domain is to assume periodicity at some predetermined wavelength along this open direction. The method used for the numerical solution of this problem is Fourier expansions for the periodic direction with Legendre spectral element discretisation for the two inhomogeneous directions. In order to maintain the separability of the pressure operator in the two inhomogeneous directions, the time marching scheme is fully explicit. This limits the highest Ra number that can be simulated due to time step limitation from the diffusive part of the problem. A related problem is the time step limitations due the collocation point distribution within each element. This is because the main flow direction is in the plane of the spectral element grid with the smallest grid size being determined by near wall diffusion. It turns out that in a number of locations, specially near the corners, the Courant limit imposes severe time step limitations. The highest Ra attained with this method is 3×10^8. The flow is unsteady but not turbulent. Figure 31 shows the instantaneous temperature field in a cross section of the natural convection in a 2:1 cavity with one homogeneous (periodic) direction. The number of collocation points is 64 in the homogeneous direction and 211×311 in the inhomogeneous ones. This is about the limit of what can be achieved with this particular combination of space and time schemes and computer resources provided by EPF-Lausanne.

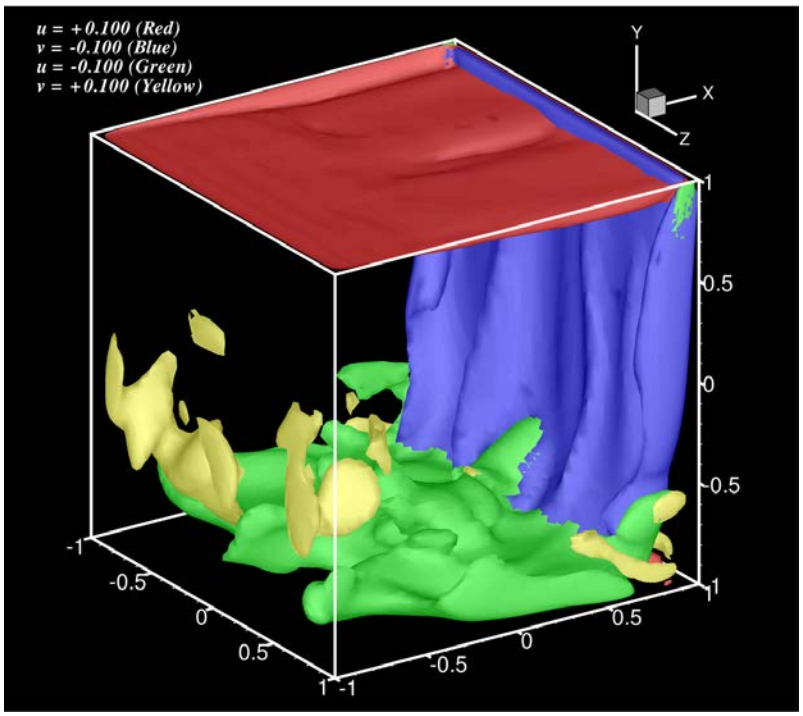

Figure 32: *Instantaneous u and v velocity isosurfaces ($u/U_o = \pm 0.1$ and $v/U_o = \pm 0.1$).*

2. A Chebyshev collocation method with a projection-diffusion algorithm has been validated in the range of Ra up to 10^6. The agreement with published data is very good. With this code, the time step limits is less stringent and it is therefore possible to tackle higher Ra numbers. This will allow simulations into the turbulent regime.

3. From the previous large user project (the DNSTLDCC project, Direct Numerical Simulation of Turbulence within a Lid-Driven Cubical Cavity), three databases at high Reynolds numbers (12000,18000 and 22000) has been generated , and statistics on meaningful sample are still currently analysed see Figure 32, [2, 7]. It turns out that the statistics for the case of Re=22000 require much more longer sample than the one at Re=18000. The sizes of the databases are of the order of 1.7 Tbytes (Re=18000) and 4.2 Tbytes (Re=22000). Those databases are also used in the framework of the large eddy simulation (LES) to validate filtering approaches and a priori / a posteriori simulation tests [6].

4. Eigenvalues analyses for the Stokes operators have been carried out. The scope of the present work is to provide the first deep insight into the Stokes eigenspace in the square [3, 4].The eigenvalues and eigenmodes are accurately computed by two different means, namely, a Chebyshev Projection-Diffusion solver and a Galerkin Reid-Harris expansion of the stream function. The symmetries which underlie the eigenmode patterns are also identified. The spectra evolution laws are in excellent qualitative agreement with the theoretical asymptotic predictions, $\lambda_k \simeq k + \mathcal{O}(\sqrt{k})$. The slopes are reported here and are found to be specific to the eigenmodes symmetry family. The dynamic equilibria are analyzed and show a linear relationship between the vorticity and the stream function in the core of the eigenmodes. These features of the Stokes eigenmodes confined in the square are shared by the fully periodic Stokes eigenmodes.The knowledge and interpretation of the Stokes

eigenmodes in the square should thus bring an interesting point of view over the resulting dynamics of 2D closed flows, complementary to what is well known regarding the inviscid regions. Analyzing the 3D Stokes eigenmodes, in the cube for instance, will likely provide valuable understanding elements on realistic flows.

5. An extension to higher-order direct Stokes solvers with or without temporal splitting has been investigated numerically [5]. The temporal stability and effective order of two different direct high-order Stokes solvers are examined. Both solvers start from the primitive variables formulation of the Stokes problem, but are distinct by the numerical uncoupling they apply on the Stokes operator. One of these solvers introduces an intermediate divergence free velocity for performing a temporal splitting while the other treats the whole Stokes problem through the evaluation of a divergence free acceleration field [1]. The second uncoupling is known to be consistent with the harmonicity of the pressure field ([1]). Both solvers proceed by two steps, a pressure evaluation based on an extrapolated in time (of theoretical order J_e) Neumann condition, and a time implicit (of theoretical order J_i) diffusion step for the final velocity. These solvers are implemented with a Chebyshev mono-domain and a Legendre spectral element collocation schemes. The numerical stability of these four options is investigated for the sixteen combinations of (J_e, J_i), $1 \leq J_e, J_i \leq 4$. The common result is that the schemes are unconditionally stable for $J_e \leq 2$, whereas a time step criterion of explicit type occurs –$\Delta t < \mathcal{O}(N^{-4})$–, when $J_e > 2$, slightly less restrictive for the consistent scheme than for the other. The effective time orders are then measured with $1 \leq J_e \leq 2$ and $1 \leq J_i \leq 4$. For the consistent solver the effective and expected time orders are in excellent agreement, and some discrepancies occur for the other scheme which turns out to provide slightly more accurate orders.

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Project title: **Proton transfer and hydrogen bonding in solvent clusters and nucleic acid base pairs: theory and dynamics**

Project leader: S. Leutwyler[1]

Researchers: A. Müller[1],
Ch. Tanner[1],
C. Manca[1],
H. M. Frey[1],
M. Meuwly[2]

Institutions: [1]Department of Chemistry and Biochemistry, University of Bern
[2]Department of Chemistry, University of Basel

Description

Our Large User Project is divided into sub-topics aimed at complementing laser spectroscopic experiments on hydrogen-bonded clusters in supersonic beams with state-of-the art quantum chemical calculations. Other sub-topics provide deeper understanding of proton transfer energetics and dynamics at the molecular level.

Subproject A: Proton transfer in clusters
The azaaromatic molecule 7-hydroxyquinoline (7HQ) has two potentially reactive groups that can serve as either a proton donor or acceptor. In 7-HQ·$(NH_3)_n$ clusters, PT transfer can occur toward and along a network of ammonia molecules, whereby the cluster can act as a proton acceptor and/or a proton wire. The occurrence or non-occurrence of proton transfer depends on the electronic state (S_0 or S_1) and on the cluster size [1, 2].
For the n=3 cluster, we have characterized the entrance channel, reaction threshold and mechanism of an excited state H atom transfer reaction along a unidirectionally hydrogen bonded "wire" -O-H$\cdots$NH$_3\cdots$NH$_3\cdots$NH$_3\cdots$N. Excitation of supersonically cooled 7HQ·$(NH_3)_3$ to its vibrationless S_1 state produces no reaction, whereas excitation of ammonia-wire vibrations induces H atom transfer with a reaction threshold at ≈ 200 cm^{-1}. Ab initio calculations show that proton and electron movement along the wire are closely coupled. The rate-controlling S_1 state barriers arise from crossings of a $\pi\pi^*$ with a Rydberg-type $\pi\sigma^*$ state, see Figure 33 [1, 3, 4]. For the n=2 cluster, no reaction is observed, even with additional excitation energy of 900 cm^{-1}. CIS calculations have been performed on the n=2 and n=3 clusters to understand the effect of the wire length on the energy profile of the reaction. The enol$\rightarrow$ keto reaction is always exoergic, and the barrier for H transfer to the proximal ammonia controls the reaction kinetics [4].

Subproject B: Structure, intermolecular vibrations and binding energies of small solvent clusters
We are currently investigating the structural and vibrational properties of several isomers of the 1-naphthol·$(NH_3)_n$, $n = 3, 4$ and 7-hydroxyquinoline·$(NH_3)_2$ clusters, using correlated electronic structure methods, both density functional (PW91, B3LYP) and MP2. $S_1 \leftarrow S_0$ excitation leads to contractions of the chromophore-solvent hydrogen bonds, indicating that H bond contractions in the excited state are prerequisite for the S_1 state proton transfer processes that occur in the larger clusters. The goals are to determine the cluster structure based on the experimental rotational constants [5] and to assign the experimental vibronic spectra [2, 3, 5, 6].

Subproject C: Hydrogen bonding in nucleobase pair analogues [7, 8, 9]
For the nucleobase pair analogue $(2\text{-pyridone})_2$ [as a mimic of $(\text{uracil})_2$], MP2 benchmark cal-

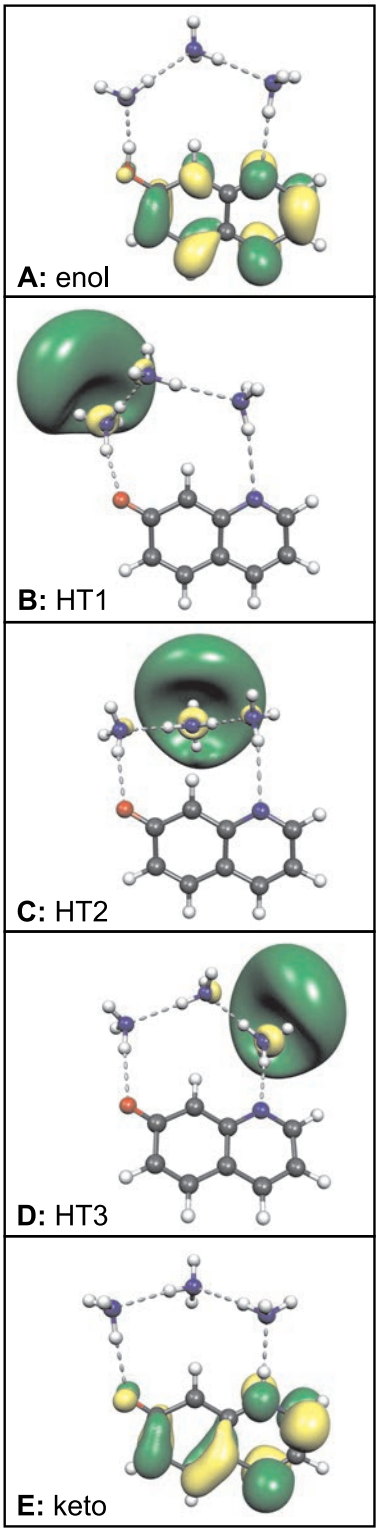

Figure 33: *Evolution of the singly occupied molecular orbital that contributes dominantly to the S_1 excited state for successive hydrogen atom transfer steps along the ammonia wire.*

culations with complete basis set extrapolations for the binding energy have been performed [7]. The PW91 and B3LYP density functionals yield excellent agreement with observed rotational constants and intermolecular frequencies [7]. We are also investigating dimers containing one canonical nucleobase, such as 2-pyridone·X, where X = uracil, thymine, 5-fluorouracil [8]; density functional and MP2 methods were employed to calculate dimer geometries, inter- and intramolecular harmonic frequencies and binding energies that can be compared to experiment.

Subproject D: Water clusters
We performed an ab initio theoretical study of the large-amplitude flipping vibrations of the $(H_2O)_6$ and $(D_2O)_6$ Cage hexamers, which exhibit double-minimum potentials along the flipping coordinates [10].

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Project title: **Quantum Chemical Investigations of Cyclization Reactions Involving Cationic Species**

Project leader: J. Mareda

Researchers: J. Mareda

Institutions: Department of Organic Chemistry, University of Geneva

Description

Cation-olefin cyclizations are among the most important and also the most complex carbon-carbon bond forming reactions. In order to achieve this cyclization the substrate has to be preorganized so that the cationic center and olefin are properly aligned. A number of enzymes and catalytic antibodies achieve the spectacular biosynthetic results often with a very good degree of stereo control via the catalysis of cationic cyclizations. While such catalysis is widespread in the biogenesis of complex natural products, their use in synthesis is possible simply by solvolysis of an appropriate substrate. While the cyclization products might differ between the antibody catalyzed and the solvolysis pathway, both types of reaction are supposed to involve the same key intermediates: protonated cyclopropanes.

In the present project we undertook a detailed investigation of the cation-olefin cyclizations, which are proceeding via the solvolytic mechanism. For the potential energy surface investigations it is important a) to model the leaving group by an appropriate functional group and b) to take into account the solvent effects. The protonated alcohol is proposed as the model of the leaving group, for the reaction of the heterolytic cleavage of C-O bond. This approach is aimed at identifying the initial cationic intermediates that are formed in the solvolysis reaction. Within this project the behavior and properties of the cationic species in presence of explicit solvent molecules were modeled with the quantum methods.

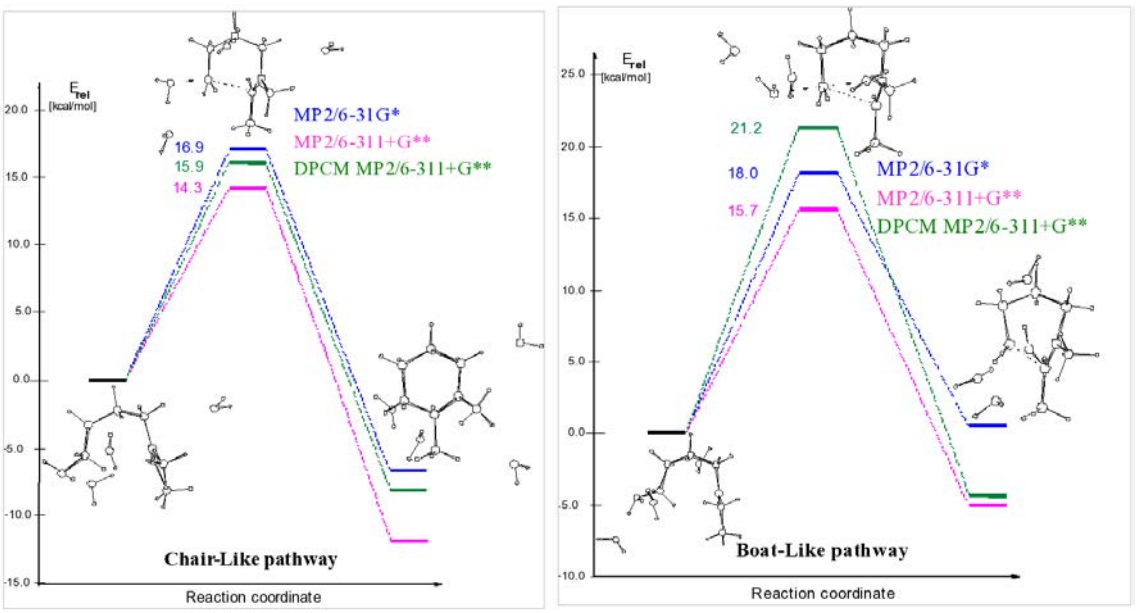

Figure 34: *Schematic energy reaction path for solvolysis of protonated cis-5,6-dimethyl-5-hexenol water cluster systems, optimized by MP2 method and combined with DPCM model*

This methodology was further improved by combining the fully optimized water-cation cluster geometries with the reaction field model where a continuous dielectric field is used to simulate the bulk of the solvent. This method gives access to a detailed studies of interactions between the reactive intermediates and the solvent molecules within the first solvation shell since they are treated explicitly. Our research indicates that the modeling taking into account the explicit solvent molecules in the combined explicit-continuum approach is the method of choice for investigations of reaction pathways for solvolysis reactions, where the reactive intermediates such as carbocations and protonated cyclopropanes are involved. The performance of methods such as Mller-Plesset, ONIOM, and mPW1PW91 using several different basis sets is evaluated in this project.

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Project title: **Electronic Structure Calculations for Molecular Dynamics Simulations of Iron-containing, reactive Centers of Biomolecules**

Project leader: M. Meuwly[1]

Researchers: D. Nutt[1],
M. Karplus[2,3]

Institutions: [1]Chemistry Department University of Basel, Switzerland
[2]Université Louis Pasteur, Strasbourg, France
[3]Harvard University, Cambridge, Massachussetts, USA

Description

Iron containing, reactive centers play an eminent role in a wide range of processes in biological systems. They include - amongst others - ligand binding (such as in myoglobin or in cytochrome P450cam) or electron-coupled proton transfer where iron-sulfur clusters are involved. Iron containing systems represent a class which are amenable to meaningful calculations particularly at the density functional level. In conjunction with molecular dynamics (MD) simulations detailed structural and dynamical information can be gained. Such an approach is taken in the present project.[1, 2]

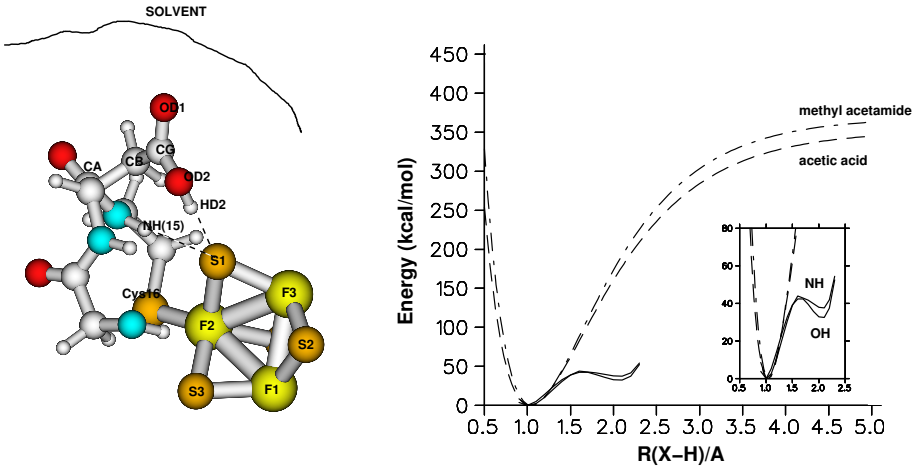

Figure 35: *Active site of Ferredoxin I (left) used in the ab initio calculations. Further calculations will include SCH_3 groups at F1 and F3. Calculated potential energy curves (right) for HD2- and NH(15)-transfer to S1. The PT curves are compared to abstraction of protons from related model compounds.*

Achievements

Electron Coupled Proton Transfer in Ferredoxin I: Using molecular dynamics simulations the role of internal water molecules in the electron-coupled proton transfer from Asp15 to a buried [3Fe-4S] cluster was established.[1] Subsequently, we assessed the possibility for different hydrogen atoms/protons to transfer to the [3Fe-4S] cluster (see Fig. 35).[2] Using UB3LYP/6-31G** calculations we found that transferring the proton from NH(15) to [3Fe-4S] or from HD2(15) to

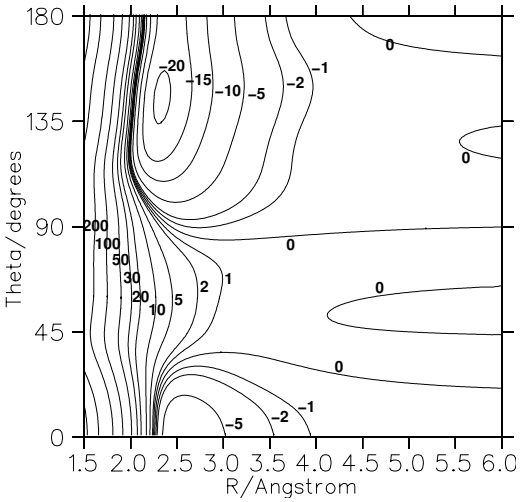

Figure 36: *Potential energy surface for the Fe-NO interaction fitted to the ab initio data. The coordinates are the distance between Fe and the center of mass of NO and the Fe-N-O valence angle.*

[3Fe-4S] involves static barriers of approximately 40 kcal/mol (see Fig. 35).[2] *Ab initio* calculations were also used to calculate the nuclear charges on the reduced and oxidized [3Fe-4S] clusters which were subsequently used in MD simulations.
The MD simulations showed that - contrary to the interpretation of experimental results[3] - other hydrogen atoms than OD2(Asp15) are more likely to *directly* transfer to the buried [3Fe-4S] cluster.[4] However, in most cases abstraction of the proton alone is not likely to occur since previous protonation is required (as in the case of HN(Asp15)) because $pK_a \approx 10$ for main chain NH.[4] Another possibility is that a water molecule can enter the active site around the [3Fe-4S] cluster and serve as a proton relay between the carboxylic end of Asp15 and the cluster. We assessed the stability of internal water molecules in 7FD1 and its mutant 1D3W. In both systems a water molecule can be stabilized.[1] Furthermore, in native 7FD1 the water molecule can escape the active site on the time scale of the MD simulations (1ns) which shows that water molecules also can enter the cavity. Since no escape of water was found for 1D3W, water penetration into the active site is likely to contribute to the rate determining step.
NO Rebinding in Myoglobin: The potential energy surface for NO interacting with heme in its ground and electronically excited state has been calculated using UB3LYP/(VTZ/3-21G*) calculations.[5] To describe the potential energy surface two coordinates were used: the distance R between the center of mass of NO and the angle θ between $\vec{R}$ and $\vec{r}$, the distance between the N and O atom. The total energies for the bound state (^2A) were fitted as a function of R and θ to an expansion

$$V(R,\theta) = \sum_{\lambda=0}^{10} V_\lambda(R) P_\lambda(\cos\theta) \tag{1}$$

A graphical representation of the interpolated surface is shown in Fig. 36. The global minimum is about 24 kcal/mol below dissociation and occurs for the Fe–NO configuration. The secondary minimum is for linear Fe–ON. Since for the bound state the Fe atom is known to be close to or in the porphyrin plane the potential energy surface was calculated for $d = 0$, where d is the distance of the Fe atom from the porphyrin plane.

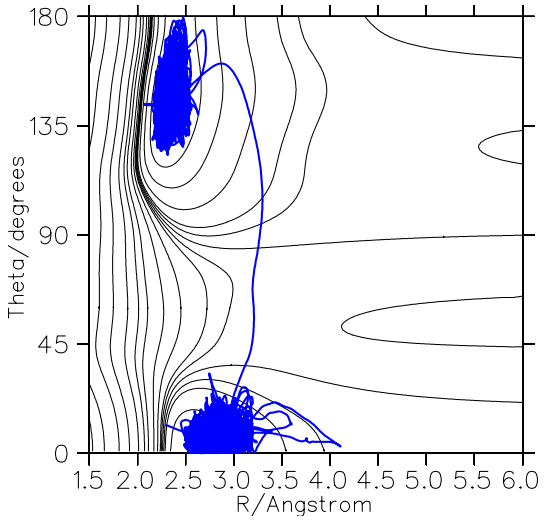

Figure 37: *Projection from a 250ps trajectory at 300K onto the potential energy surface. The trajectory started from the less stable Fe–ON configuration and crosses the barrier to finally end up in the more stable Fe–NO configuration.*

Initially, it was of interest to investigate the bound-state dynamics using the intermolecular potential energy surface for the motion of NO bound to Fe. Starting from an equilibrated trajectory of bound NO using the old molecular mechanics force field (harmonic Fe-N bond and harmonic Fe-N-O angle terms) 250 ps of molecular dynamics simulation on the new potential energy surface were run. The trajectory started from the energetically less favoured Fe–ON configuration. Since the barrier for crossing to the Fe–NO structure is only 8 kcal/mol this transition is possible at ambient conditions as shown in Fig. 37). Also, large scale excursions in the Fe–ON configuration are possible which are not seen for Fe–NO. Recrossing from the global minimum was not observed on the time scale of the simulation.

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Project title: **Minerals and Planetary Materials**

Project leader: A. R. Oganov[1]

Researchers: P. I. Dorogokupets[2]
D. Y. Jung[1]

Institutions: [1]Laboratory of Crystallography, ETH Zürich
[2]Institute of the Earth's Crust, Irkutsk, Russia

Description

Our project is concerned with the prediction of structures and properties of the materials of planetary interiors and is divided into two parts -1)minerals of the deep Earth, 2)materials of giant planets. Our simulations are based on density functional theory; their ultimate goal is to advance the understanding of the state of matter in deep planetary interiors and complex geological processes taking place therein. At this stage we concentrate on the minerals of the Earth's lower mantle, which makes up 53 vol.% of the Earth. In near future we plan to explore fluid H-He mixtures dominating the composition of Jupiter and Saturn. There have been several important themes in our recent work:

A. High-pressure stability of the Earth's mantle minerals.
Using density-functional perturbation theory we have studied lattice dynamics and high-pressure phase diagrams of MgO [1], SiO_2 [2], and $MgSiO_3$ [3]. We find [1] that MgO remains in the NaCl-type structure at all conditions within the Earth. The calculated phase diagram of SiO_2 [2] allowed us to predict the depths of seismic discontinuities that would appear within the lower mantle if SiO_2 phases were present in significant amounts. Since these depths (1410 and 2210 km) do not correspond to any observed discontinuities, one can infer that SiO_2 polymorphs are not present, at least as major phases, in the lower mantle. $MgSiO_3$ perovskite is found [3] to be stable with respect to decomposition into oxides, with pressure and temperature only increasing its stability. Ab initio molecular dynamics simulations confirm that within the Earth's lower mantle $MgSiO_3$ perovskite is orthorhombic (Pbnm) - see Fig. 38. We have also looked at perovskite-structured materials, focussing on lattice dynamics [4] and energetics [5]. For $CaSiO_3$ perovskite the tetragonal and orthorhombic structures are energetically very similar and slightly more favourable than the idealised cubic structure. The calculated [5] enthalpy of decomposition of this mineral into the oxides is so large (1.21 eV at 40 GPa, 1.76 eV at 120 GPa) as to effectively rule out its decomposition within the lower mantle. These and other findings, putting mineralogical models of the Earth's mantle on a firmer basis, have been summarised in a review [6].

B. Equations of state of minerals.
Equations of state of minerals play a central role in modelling the Earth's interior. The most difficult properties are the Gruneisen parameter and intrinsic anharmonicity. We have developed a method to extract these from molecular dynamics simulations [7]. Furthermore, we have developed a quantum theory of intrinsic anharmonic effects based on thermodynamic perturbation theory [8, 9]. Performing ab initio molecular dynamics simulations of the thermal equation of state of MgO with pseudopotential and all-electron PAW methods, we found similar results, except at very high pressures, where the differences become significant. Theoretical Gruneisen parameters and intrinsic anharmonicity parameters are in very good agreement with the values that we extracted from experiment using our procedures for the simultaneous treatment of thermodynamic databases and experimental equation of state data.

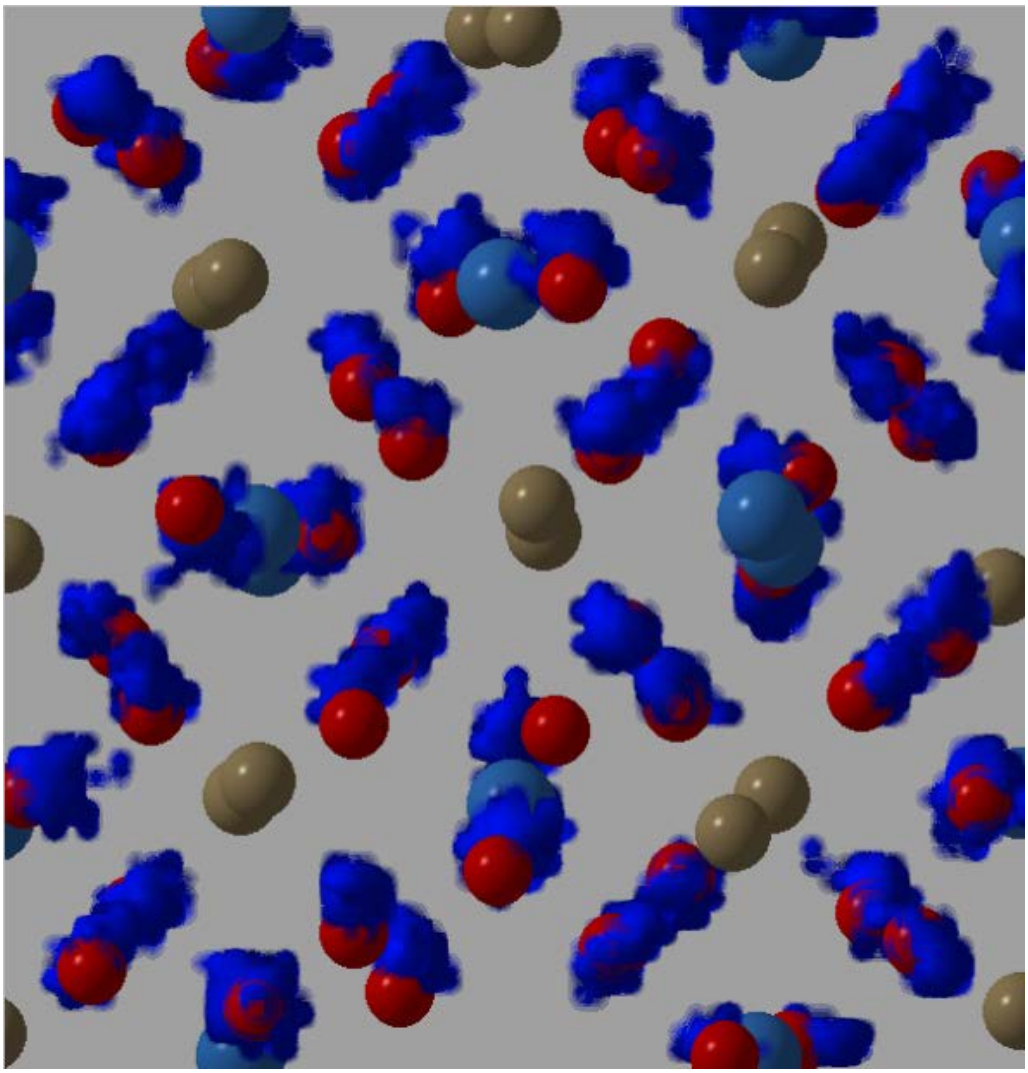

Figure 38: *Snapshot of a constant-NVT ab initio molecular dynamics run for $MgSiO_3$ perovskite (P=88 GPa, T=3500 K). The starting cubic structure spontaneously distorts into the orthorhombic one, as can be seen from the splitting of oxygen positions. Spheres: grey - Mg, blue - Si, red - O. Blue "clouds" trace the trajectories of the O atoms and show the splitting of the positions of O. Visualisation done with the STM3 package of M. Valle and J. Favre (CSCS).*

C. Effect of Fe impurities on the properties of mantle-forming minerals.
We are interested in the effects of Fe on the equations of state of MgO and $MgSiO_3$ - these are still largely unknown. In particular, the possibility of an electronic transition of Fe^{2+} and its possibly large effects on the properties are of interest. It is known, however, that standard DFT does not describe well the electronic structure of transition metal oxides and silicates. Therefore, we use the DFT+U approach, where electron correlations missing in standard DFT are included empirically, using parameters U and J. In agreement with recent experiments we find a strongly first-order electronic transition in (Mg,Fe)O, and the pressure at which this transition occurs (˜50 GPa) is only weakly dependent on U and J. At the same time, this transition pressure is stronly dependent

on the concentration of Fe and its distribution over lattice sites. The possibility of a first-order electronic transition of Fe impurities within the lower mantle can have important implications for seismic heterogeneity and rheology of the mantle. This work is in progress.

Achievements

The calculated phase diagrams of MgO, SiO_2, $MgSiO_3$, $CaSiO_3$ [1, 2, 3, 4, 5] support the traditional mineralogical models of the Earth's lower mantle. We have shown that the principle of close packing (that has long been considered as a cornerstone of mineral crystal chemistry) can, counter-intuitively, break down under pressure even at the absence of electronic transitions or coordination number changes. We have shown how to separate quasiharmonic and intrinsic anharmonic effects in molecular dynamics simulations and did so using ab initio MD for MgO [7] and developed thermodynamic perturbation theory of anharmonic effects [8, 9] and applied our formalism in joint treatment of experimental thermodynamic databases and equations of state to the reference substances Cu, Ag, and MgO, which has led us to a new calibration of the ruby pressure scale [10].

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Project title: **Global Climate Change:**
Modelling Atmosphere/Ocean Variability on Decadal Time Scales

Project leader: M. Wild, A. Ohmura

Researchers: A. Roesch
P. Tschuck
C. Schneeberger

Institutions: Institute for Atmospheric and Climate Sciences ETH Zürich

Description

The most powerful tools to investigate the potential impact of human activities on the Earth's climate are three dimensional numerical models of the global climate system. Such models are used in the "Global Climate Change: Modelling Atmosphere/Ocean Variability on Decadal Time Scales" to investigate the response of the Earth's climate to natural and human induced perturbations. Global climate modelling at ETHZ is part of the National Center of Competence in Climate Research (NCCR Climate[14]). The emphasis is on the simulation of present and future climate, using the latest model version of the global climate model developed at the Max Planck Institute for Meteorology in Hamburg (ECHAM5). Thanks to the generous computational resources allocated to this project by CSCS scenario runs with a very high grid resolution over the entire globe can be carried out. This allows for an improved representation particularly of topographic effects such as terrain induced precipitation. Currently scenarios for the late 21th century with increased levels of atmospheric greenhouse gases are underway. Our focus is on the near surface climate from global scale down to European and Alpine scales.
Particular emphasis is placed on the surface energy and water exchange processes and their potential changes under increased greenhouse forcing. Of interest in this context is, for example, the change in the atmospheric thermal emission radiating back to the surface, which is the most direct effect that can be felt at the surface from a change in atmospheric greenhouse gas composition. A further focus of the project is placed on the impact of greenhouse warming on the cryosphere (snow, mountain glaciers, polar ice sheets) and their effects on the sea level. The high spatial resolution of the scenarios allows for better estimates of the cryospheric contribution to sea level changes.
Our experiments carried out at CSCS are designed as NCCR community scenarios and form the basis for a variety of subsequent analyses and impact studies to be carried out within other NCCR projects.

Achievements

A major advantage of global high-resolution experiments is an improved representation of topography and associated effects, such as orographically induced precipitation, which are of key importance for mountainous areas. This enables, i.a., a more realistic simulation of snow accumulation, thereby allowing for more reliable estimates of future mass balance changes on mountain glaciers and polar ice sheets, and their respective impact on global sea level (Wild IPCC TAR 2001 Chapter 11). The scenario experiments carried out with ECHAM4 T106 at CSCS posed the main experiments for the assessment of the cryosphere contribution to sea level within the IPCC third assessment report (Wild IPCC TAR 2001 Chapter 11). These experiments have been further analyzed and results of these studies have been published (Wild et al. 2003, Schneeberger et al., 2003, Huybrechts et al. 2003).

[14] http://www.nccr-climate.unibe.ch

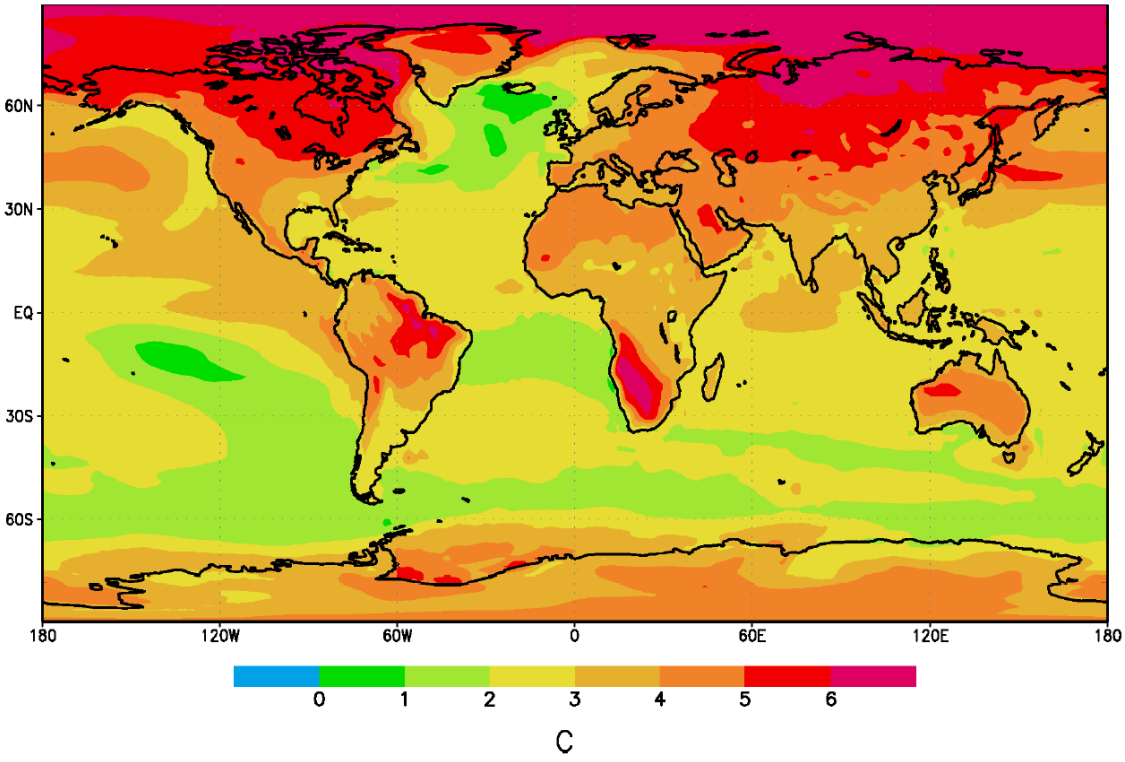

Figure 39: *Projected temperature change towards the end of the 21th century based on the Global Climate Modell ECHAM5 and IPCC emission scenario A2*

The high-resolution scenario experiments suggest, that, under 2x CO_2 conditions, mass gain may not only take place in Antarctica, but also in Greenland (Wild et al. 2003, Huybrechts et al. 2003). The net effect of the polar ice-sheets on global sea-level at the time of 2xCO_2 is thus being projected as negative, and of magnitude which may compensate for a significant part of the sea level rise induced by the melting of mountain glaciers and small ice caps, which can be also addressed with the experiments carried out at CSCS (Van de Wal and Wild 2001, Schneeberger et al. 2001, 2003). This leaves thermal expansion as dominant factor for sea level rise over the coming decades. The compensating effect, however, could fade if carbon-dioxide concentrations in the atmosphere cannot be stabilized and continue to rise above double the present values, since the associated greenhouse warming could then become large enough to induce significant melting also on the Antarctic ice sheet (Wild et al 2003).

A major research focus of the ETH group has been devoted to the investigation of radiative and surface exchange processes in Global Climate Models, which constitutes the core competence of the group. Various deficiencies in the current representation of these processes in climate models were detected and improvements suggested, as documented in a series of papers (e.g., Wild et al. 2001, Wild and Cechet 2002, Roesch et al. 2001, 2002, Sheppard and Wild 2002). It was shown, that accurate surface fluxes are critical for a realistic simulation of surface climates and for an adequate coupling of the atmospheric model component to the ocean and land surface models. This work is on an international program level integrated in AMIP (Atmospheric Model Intercomparison Project), with the AMIP Project ”surface and atmospheric radiative fluxes” (PI M. Wild).

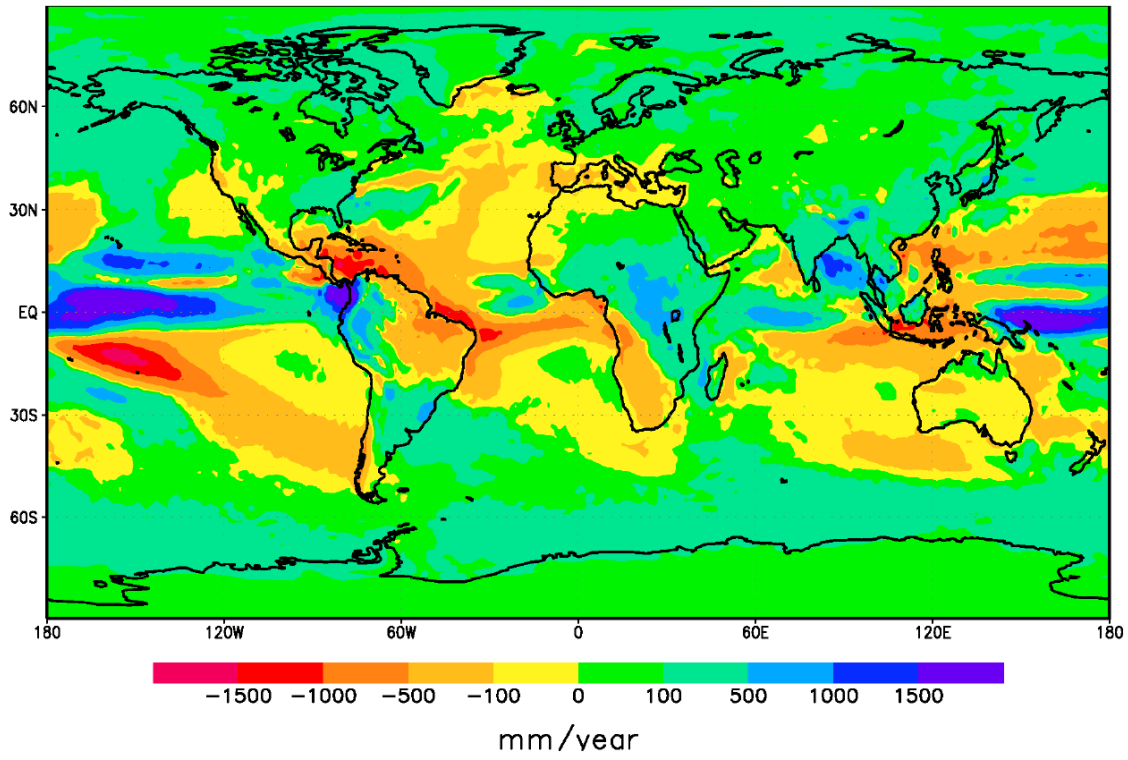

Figure 40: *Projected precipitation change towards the end of the 21th century based on the Global Climate Modell ECHAM5 and IPCC emission scenario A2*

A new high resolution version of the latest development stage of ECHAM5 (version ECHAM5.2) has been newly installed at CSCS and prepared for new time slice experimA2ents. With the coupled atmosphere ocean model ECHAM5/HOPE, ensemble experiments have been carried out at CSCS in the previous period to assess the predictability of the climate system on decadal to multidecadal timescales. On these timescales the variability of the oceanic circulation may provide a potential for climate prediction. Results suggest that the sea surface temperatures of the North Atlantic, Nordic Seas and Southern Ocean bear a predictability potential on multidecadal timescales (Tschuck et al. 2003, Pohlmann et al, 2003).

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Project title: **Experimental High Resolution Weather Forecast**

Project leader: E. Parlow

Researchers: Mathias D. Müller

Institutions: Institute of Meteorology, Climatology and Remote Sensing

Description

A state of the art numerical weather prediction model was used to compute high resolution weather forecasts for Switzerland on a daily basis. The simulations and the model were used to develop and test new parameterizations and satellite derived datasets. The daily runs were verified with observations. Skill scores of the model improved due to a new radiation parameterization and the inclusion of satellite derived NDVI and snow cover data.

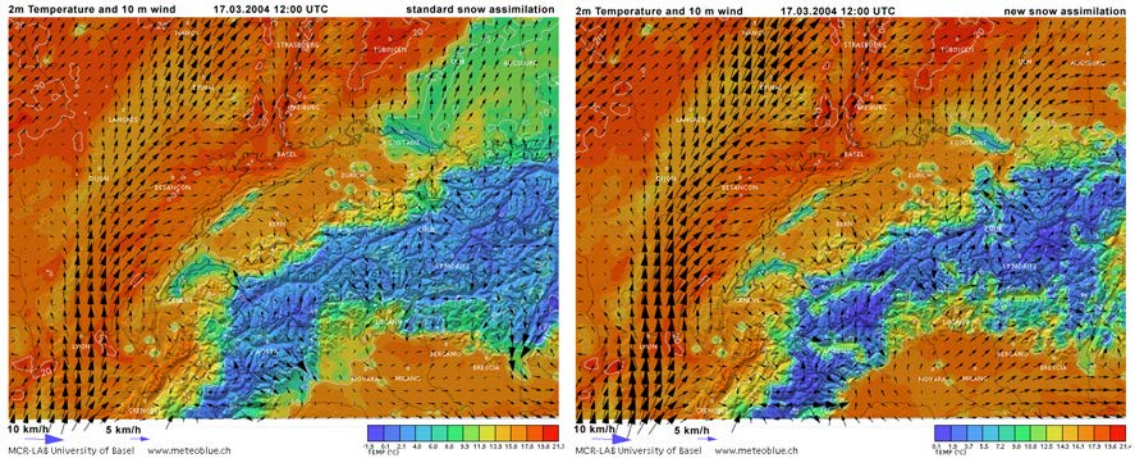

Figure 41: *Forecasted 2 m temperature and 10 m wind with and without the new snow cover.*

Achievements

The nonhydrostatic mesoscale model (NMM) of NOAA/NCEP [2, 1] was run at resolutions of 22 km, 4 km and 2 km. In cooperation with the Remote Sensing Research Group of the University of Bern, daily high resolution NDVI and snow cover data, derived from NOAA/AVHRR, were incorporated into the assimilation process and a skill improvement of the forecast has been demonstrated [4, 3]. Furthermore a gridscale and subgrid scale radiation parameterization of topographic effects for mesoscale models was developed and implemented into the 4 km and 2 km version of NMM [5]. In Figure 1 the forecast of 2 m temperature and 10 m wind with and without the new snow cover data are presented. High resolution of the new snow cover assimilation yields more realistic forecasts of the temperature field.

The skill improvement due to daily NDVI assimilation is demonstrated in Figure 2. For a 2 months period the 4 km NMM model was run in parallel, using standard and new NDVI assimilation. For each available measurement station the percentage of days with higher skill of the new NDVI dataset is indicated.

The new radiation parameterization takes into account the effects of slope angle, slope aspect, skyview restriction and shadow at the same or a higher resolution than the model grid. The computational costs of the scheme are negligible. Figure 3 shows verification scores of 2m air temperature for alpine stations with and without the new radiation parameterization on a clear sky

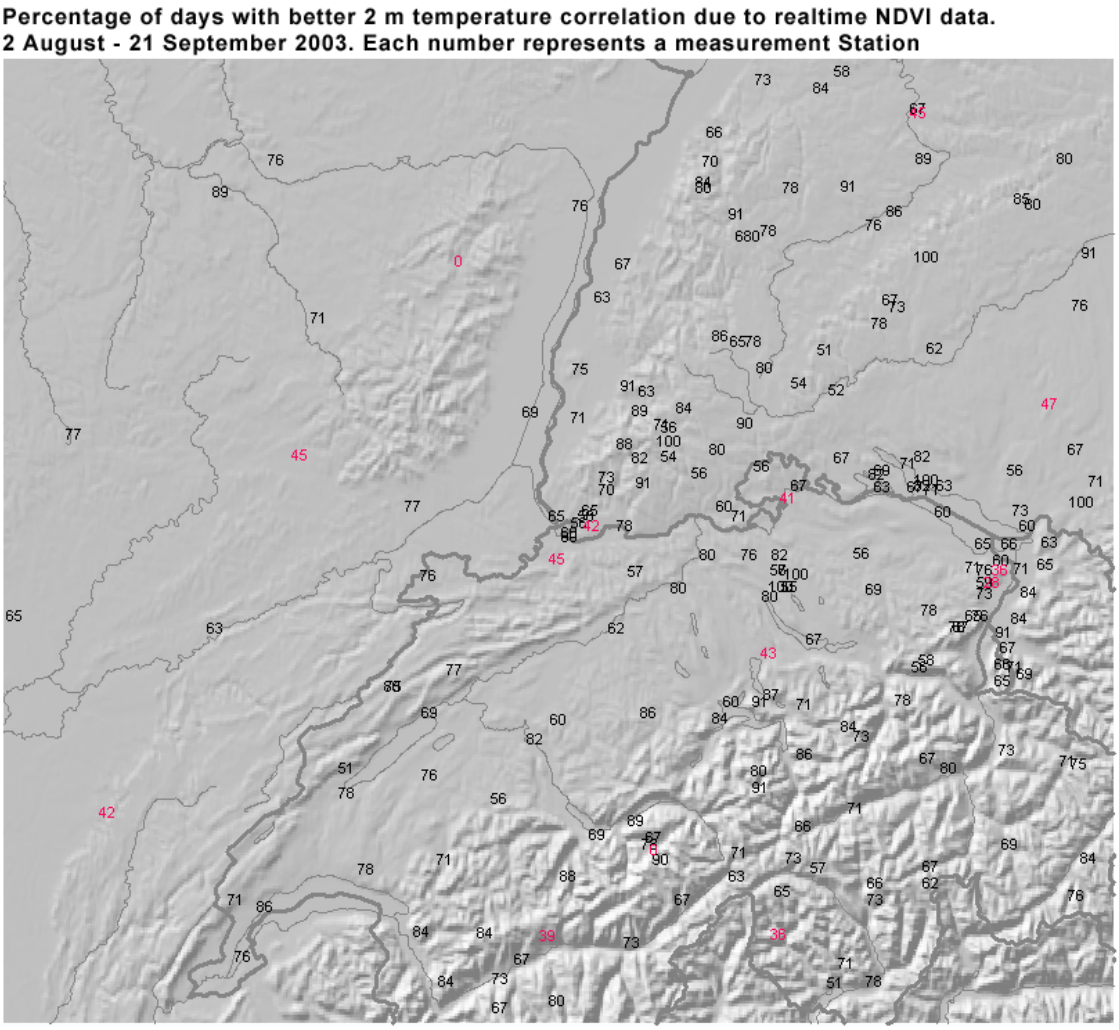

Figure 42:

situation for 22 June 2003. 2-PAR and 4-PAR are the 2 and 4 km runs with the new radiation scheme, 2-CTL and 4-CTL are with the standard radiation scheme. Clear sky winter conditions for 25 December 2003 are shown in Figure 4. Most improvement is observed at night, when restricted skyview in valleys reduces the loss of long-wave radiation yielding a smaller cold bias of the model. The more realistic treatment of shortwave radiation significantly modifies the temperature forecasts in complex terrain. In Figure 5 red areas indicate a warming on inclined surfaces facing the sun, whereas colder blue areas show the effect of shadow and inclined surfaces not facing the sun.

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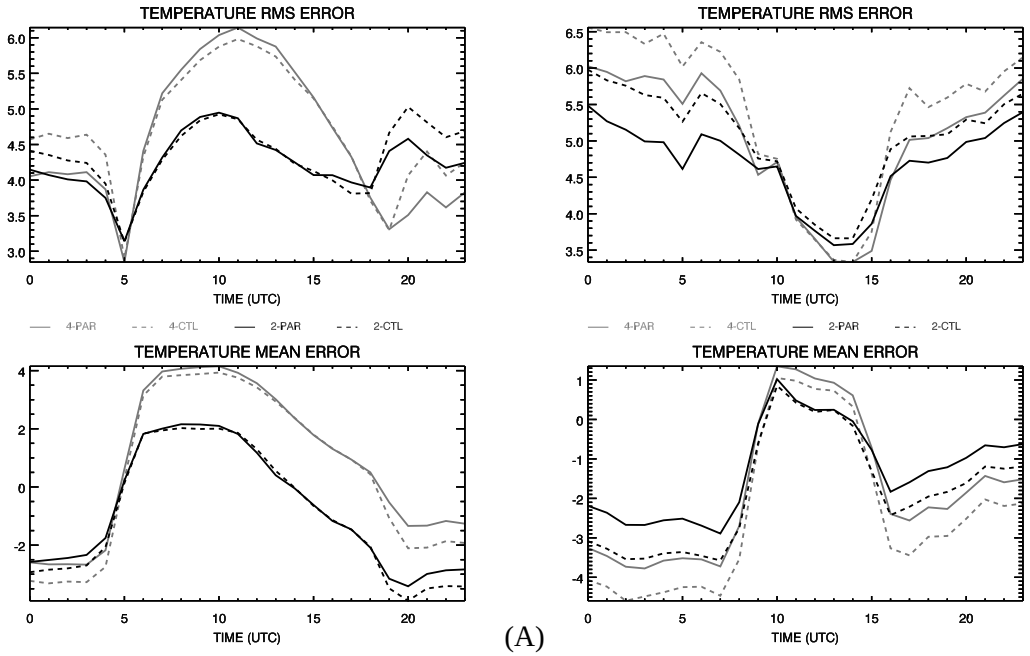

Figure 43:

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Project title: **Disordered Network-Forming Materials**

Project leader: A. Pasquarello

Researchers: A. Bongiorno
V. Dubois
L. Giacomazzi
F. Giustino
T. Oda (visiting)
Z. Sljivancanin
P. Umari

Institutions: Institute of Theoretical Physics of EPFL
and IRRMA

Description

Atomic-scale phenomena in the context of disordered network-forming systems are studied by first-principles simulation, both from the structural and dynamical point of view. The research project is composed of three subprojects:

1. *Atomic-scale processes at oxide-semiconductor interfaces* - This project intends to bring the potential of first-principles simulation to the study of semiconductor-oxide interfaces which are of interest in current electronic technology. We envisage to focus our attention on three type of interfaces: (i) the Si-SiO_2 interface, (ii) interfaces between silicon and high-κ oxides, and (iii) the SiC-SiO_2 interface. One of the main goals consists in providing an atomistic description of the mechanisms which govern the oxidation process.

2. *Vitreous systems* – Modelling approaches are developed in order to extract from experimental data detailed information regarding the structure of disordered network-forming systems (e.g. SiO_2, GeO_2, B_2O_3, $GeSe_2$, H_2O). Our approach allows us to characterize these materials by modelling their vibrational spectra from first principles: these include inelastic neutron, infrared, Raman, and hyperRaman spectra.

3. *Catalysis on nanostructured surfaces* - The goal of this project is to investigate reaction pathways which are alternative to the industrial Haber-Bosch process and which are inspired by the nitrogen fixation in the biological enzyme nitrogenase.

Achievements

During the elapsed year, the major results were obtained in the following research directions of the project:

Vitreous materials

- We have undertaken the study of the vibrational spectra of vitreous B_2O_3. These include inelasitic neutron spectra, infrared and Raman spectra. The main scope of this study was the determination of the structure beyond the first neighbor shell, which is known to be composed of a triangle with B at the center and O atoms at the corners. In particular, the focus was on determining the amount of boroxol rings which correspond to three connected triangles forming a 6-atom ring of alternated O and B atoms. Our study has revealed that the amount of O atoms occurring in boroxol rings can be quantified to be 40%. This value has been consistently obtained from the analyses of both the inelastic neutron and Raman

spectra. We are currently investigating the significance of NMR data obtained for the same material. This investigation will give rise to several publications. In progress. In collaboration with P. Umari (SNF).

- The study of Raman spectra was made possible by a computational tool we developed within this project. This tool allows the application of finite electric fields within periodic density functional calculations. We have continued the investigation of related properties of this method, such as the convergence as a function of the size of the simulation cell. In collaboration with P. Umari (SNF). Refs. [5,8,15,18,19,28].

- Using first-principles molecular dynamics, we have started the study of the dielectric properties of liquid HCl. This exploratory investigation is supposed to highlight the possibility of accessing the static dielectric constant of this liquid using the novel finite-electric field method. In fact, by evolving the molecules in a static electric field, we should be able to capture the effect related to the reorientation of the dipoles in the liquid. In progress. In collaboration with V. Dubois (SNF).

- We have continued our investigation of chalcogenides. These materials are interesting from the fondamental point of view because of their peculiar intermediate range properties. We studied in particular the charge-charge correlations in liquid $GeSe_4$. This study revealed that there appears to be a general rule which prevents charge oscillations on intermediate length scales. This observation might be of help in the understanding of the absence of any first sharp diffraction peak in the concentration-concentration structure factor found in simulations of liquid $GeSe_2$, in sharp contrast with the experimental result which shows a clear peak. Continuing. In collaboration with C. Massobrio (Strasbourg). Refs. [7,14].

- We have studied the decomposition of non-stochiometric silica upon annealing into silicon and stoichiometric silica, using a new method based on mapping Metropolis Monte Carlo simulations onto rate equations. The concentrations of all oxidation states of silicon are derived as a function of time and found to attain steady state values at long times dependent on temperature T and oxygen content x. The degree of phase separation and the sizes of particles of the minority phase are predicted as a function of T and x, enabling greater control over the size of silicon quantum dots in silica matrices. In collaboration with V.M. Burlakov, G.A.D. Briggs, and A.P. Sutton (Cambridge), and A. Bongiorno (SNF). Ref. [30].

Thin dielectric films on silicon

- Our study of the structure at the Si(100)-SiO_2 interface was extended by the generation of additional model structures of the interface. The model structures differ in the detailed bonding properties in the vicinity of the interface. Ion scattering simulations were then performed on these model structures and a detailed comparison was carried out with available experimental data. To validate the quality of such comparisons, we also considered other Si(100) surfaces, such as the Si(100)1×1:H surface and the clean Si(100)2×1 surface, for which the detailed atomic structures can be considered as known. In this way we could determine the expected degree of error between theory and experiment. The consideration of six model interfaces together with this determination of the expected error allowed us to make a strong case in the case of the Si(100)-SiO_2 interface. We arrived at two main conclusions: (i) abrupt interface models with a regular pattern of O bridges, often invoked in the recent literature, could be ruled out; (ii) we provided a precise estimate of the amount of

displaced Si atoms on the silicon substrate side of the interface. We identified two possible atomic structures which could produce the estimated amount of distortions. The first structure contains a single disordered Si layer in the upper layer of the substrate. The second structure shows an important amount of O protrusions (-Si-O-Si-) into the silicon side of the interface. In collaboration with A. Bongiorno (IRRMA, FNS), M.S. Hybertsen (Agere Systems, Bell Labs), and L. C. Feldman (Vanderbilt University). Ref. [10,12,16,23,26].

- We modelled Si $2p$ core-level shifts at Si-$(ZrO_2)_x(SiO_2)_{1-x}$ interfaces for varying Zr content x. Using a first-principles approach, we calculated Si $2p$ shifts for a model interface and for cluster models, and established the validity of a linear dependence of these shifts on both the number of second-neighbor Zr atoms and the O coordination of these Zr atoms. Applying this relation to model structures of amorphous Zr silicates generated by classical molecular dynamics, we found that the Si $2p$ line shifts to lower binding energies with increasing Zr content x, in accord with experimental data. Our results therefore support the use of the Si $2p$ shift as an indicator of the Zr content in the silicate film. In collaboration with F. Giustino (CSCS-EPFL). Ref. [2].

- In the macroscopic regime, the permittivity of two adjacent dielectrics is obtained from those of the respective bulk materials according to classical electrostatics. However, when the thickness of one component approaches the atomic scale, the resulting permittivity can only be obtained through a detailed quantum mechanical description of the electronic structure. The dielectric permittivity of ultrathin SiO_2 films has acquired importance in the context of silicon technology. While current research is focusing on the replacement of the gate oxide SiO_2 by a material of higher dielectric permittivity κ, the undesired formation of an ultrathin SiO_2 interlayer could compromise the overall permittivity of the gate dielectric. To address this issue, we introduced a novel scheme within density functional theory. We focused on the Si-SiO_2 interface because of its immediate interest in silicon technology. Using atomistic model structures, we calculated both the static and high-frequency dielectric permittivities of ultrathin SiO_2 films on silicon, for oxide thicknesses up to 12 Å. First, we show that the calculated permittivities are accurately reproduced by a classical three-layer model. We then rationalize this finding by determining the microscopic polarization profile across the interface. An analysis of the local screening based on the Berry-phase theory of polarization reveals that the dielectric transition is dominated by the chemical grading. Induced gap states are shown to play a minor role. In collaboration with F. Giustino (CSCS-EPFL). Ref. [24,25]

- We extended our first-principles study of the dielectric properties of materials with high dielectric constants to HfO_2 and TiO_2 and their crystallline silicates. These materials are currently being considered as promising substitutes for SiO_2 in future Si-based electronic devices. Our study was stimulated by other work in the literature which found important differences between HfO_2 and ZrO_2. We found instead that the structural and dielectric properties of these two materials are overall very similar. In collaboration with G.-M. Rignanese and X. Gonze (Louvain-La-Neuve). Refs. [20,29,31].

Catalysis on nanostructured surfaces

In the framework of a collaboration with the group of Prof. H. Brune at EPFL, we first studied the structural and magnetic properties of small Fe clusters deposited on a MgO(100) substrate. We found that the magnetic moments of the smallest Fe clusters underwent significant reductions with respect to the gas phase and explained this property by intracluster charge rearrangements. We then

continued this investigation investigating the reactivity supported Fe nanoclusters. We focused on the sequential adsorption of N_2 molecules on a Fe nanocluster supported by an MgO substrate. The reactivity of the nanocluster was found to be affected by both the substrate and the occurrence of preadsorbed species. While the former always gives rise to an attractive interaction, the latter can either result in an attractive or a repulsive interaction depending on the number of preadsorbates. In particular cases, the dissociation of an adsorbed N_2 molecule is found to be quenched, leading to distinctive catalytic properties. In progress. In collaboration with Z. Sljivancanin (IRRMA). Ref. [13,27]

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Project title: **Structural and electronic properties of solids and surfaces**

Project leader: M. Posternak

Researchers: N. Binggeli
G. Cangiani
S. Dommange
T. Maxisch
C. Sgiarovello

Institutions: Institute of Theoretical Physics (Prof. A. Baldereschi), EPF Lausanne.

Description

Our Large User Project is divided into two sub–topics: *"Solid surfaces and interfaces"*, and *"Dielectric and vibrational properties of semiconductors and insulators"*. During the period under consideration, the main activity has been focused on the former sub–topic, whose results are described in the following:

The study of the surface morphology dependence of the ionization potential of GaAs has been pursued. We have focused our activity on ab–initio calculations of the GaAs(100)(8x2)c–(4x2) surface reconstructions, *i.e.*, the 2β and the ξ structures. The corresponding computational work has been rather heavy due to the huge size of the supercells. In order to reduce the computational load, we have decided to saturate the dangling bonds on one side of the GaAs slab with hydrogen atoms. This reduces the slab size and, accordingly, the number of plane–waves which are needed in the computation in order to achieve satisfactory convergence of the results; however, the presence of two inequivalent surfaces and the use of periodic boundary conditions produce an undesired electric field in the system, which must be evaluated through a linear fit of the potential both in the slab and in the vacuum separating consecutive slabs, in order to be able to extract from the crystal potential the potential step at the surface. The converged values of the ionization potential are 4.85 ± 0.03 eV and 5.04 ± 0.03 eV for the 2β and the ξ atomic arrangements, respectively. These values should be compared with that, previously calculated by us, of the ionization potential of the GaAs(100)c–(4x4) reconstruction, which is 5.09 ± 0.03 eV. These results are globally consistent with the trends experimentally measured for the work function of different GaAs(100) surface reconstructions [W. Chen *et al.*, J. Vac. Sci. Tech. B **10**, 1886 (1992)].

In order to complete our investigation of the ionization potentials of GaAs, we looked for a model which could reproduce the ab–initio results calculated for GaAs(110) and several atomic geometries of GaAs(100), and which could be used to qualitatively predict the changes of the ionization potential corresponding to general modifications of the surface atomic structure. The simple model described in the previous report does not apply to all reconstructed surfaces, and requires a generalization. The original model consists in separating the bulk charge in neutral As– and Ga–sp^3 building blocks (which carry no dipole nor quadrupole, so that no surface anisotropy arises), and then allowing interatomic electron transfers in order to satisfy the electron counting rule [M. D. Pashley, Phys. Rev. B **40**, 10481 (1989)]. By explicitly introducing into the model an appropriate "bulk–like" reference system for each surface atomic geometry, it has been possible to obtain a scheme which reproduces the ionization potential trends for surfaces with different crystallographic orientations and, for a given orientation, reconstructions with very different structural patterns. The generalized model has been applied to all GaAs reconstructed surfaces that have been considered in ab–initio calculations. It provides a satisfactory general description of the ion-

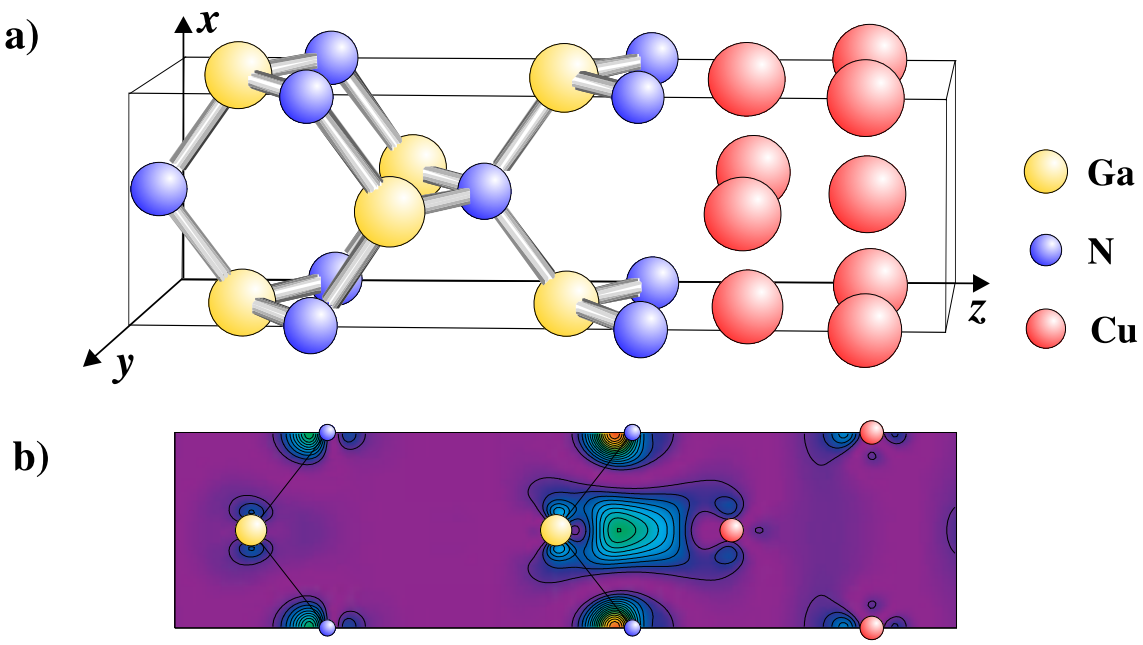

Figure 44: *Upper panel: Atomic structure of the abrupt, N-terminated Cu/GaN(001) interface. Lower panel: Contour plot, in the basal plane including interfacial Ga, N and Cu atoms (yz-plane), of the probability density of the localized interface state at the* ***J****-point of the 2D-BZ.*

ization potential trends with surface atomic geometry, and highlights the dominant mechanisms behind the observed potential changes. A manuscript reporting all the ab–initio and generalized–model results has been submitted to Phys. Rev. B for publication. The PhD thesis corresponding to this research activity has been successfully defended by Dr. Claudia Sgiarovello on September 12, 2003.

We have also performed a theoretical study of the physical characteristics of metal/semiconductor junctions. Using first principle pseudopotential calculations, we have investigated the nature of electronic states with energies within the semiconductor band gap of representative abrupt, defect–free, anion–terminated metal/III–V interfaces. Namely, we focused on Al contacts to GaAs(001), AlAs(001) and cubic GaN(001) as well as on Al, Au and Cu junctions to cubic GaN(001).

Recent advances in Schottky barrier concepts have emphasized the possible relationship between interface states and the formation of the Schottky barrier. We have studied the atomic–scale mechanisms responsible for interface states as well as their role in the Schottky barrier formation process. At As–terminated Al/GaAs(001)[T. Maxisch *et al.*, Phys. Rev. B, **67**(12), 125315 (2003)] and Al/AlAs(001) [T. Maxisch *et al.*, Solid State Commun. **126**(5), 265 (2003)] junctions, resonant and localized interface states occur at the J point of the interface 2D Brillouin zone near the Fermi energy in the semiconductor midgap region. They correspond to intermetallic bonds between the outermost cation atoms of the semiconductor and the interfacial Al atoms of the metal. These interface states derive from an interaction between localized states of the Al(001) surface and semiconductor conduction band states, mediated by localized states of the unreconstructed, As–terminated semiconductor (001) surface. Our results indicate that interface states of the intermetallic, bonding–like kind could play an important role in the transport properties of

metal/$Al_xGa_{1-x}As$ junctions.

We have also investigated the electronic structure of Al, Au and Cu junctions to cubic, N– terminated GaN(001). The localized interface state reported for As–terminated Al/GaAs(001) and Al/AlAs(001) junctions occurs also at metal/GaN interfaces under the condition that atoms on the outermost atomic plane of the metal are placed in front of the outermost semiconductor cation. This indicates that the formation mechanism of this interface state is a very general one. In contrast to Al/$Al_xGa_{1-x}As$ junctions, these states occur at energy much larger than E_F for the contacts to GaN. Thus, they are not expected to contribute significantly to the electronic transport of the latter interfaces. However, a large number of interface states attributed to *d*–type orbitals occur over a wide energy range including E_F at contacts of noble metals to GaN(001). The PhD thesis corresponding to this research activity has been successfully defended by Dr. Thomas Maxisch on November 19, 2003.

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Project title: **Computer Modeling of the Molecular Mechanisms Involved in Light Detection**

Project leader: U. Röthlisberger

Researchers: L. Guidoni, U. Röhrig, M. Sulpizi

Institutions: Laboratory of Computational Chemistry and Biochemistry, EPF Lausanne

Description

Time-dependent density functional theory (TDDFT) is an accurate and fast method to investigate spectroscopic properties, like absorption and fluorescence spectra, of relatively large molecules. The extension of this technique to hybrid quantum-classical (QM/MM) calculations is a further step towards the description of large and realistic systems, such as fluorescence probes in solution and chromophores in a protein environment. Our QM/MM scheme has been coupled to the linear-response TDDFT implementation [1] in the Car-Parrinello molecular dynamics code (CPMD) [2], allowing us to perform QM/MM molecular dynamics simulations in electronically excited states. We have extensively tested and applied both the restricted open-shell Kohn-Sham (ROKS) [3] and the TDDFT QM/MM methods to the calculation of spectral properties of chromophores in condensed phase. [4, 5, 6, 7, 8]

Achievements

As a first promising test case we applied our approach to the study of the solvent effects on the ground state and on the first excited singlet state of acetone in water The experimentally observed blue shift of the absorption energy in passing from gas phase to aqueous phase is well captured, and excited state MD simulations carried out with ROKS yield the relaxation of the solute and the rearrangement of the solvent structure on a picosecond timescale. [4, 5]

The optical properties of aminocoumarins, a class of organic compounds with extensive and diverse applications, have been studied in vacuo, in water, and in acetonitrile. In vacuum, the calculated absorption spectra of three selected aminocoumarin compounds (Fig. 45A) show an increasing red shift with increasing degree of alkylation of the amino group ($C151 < C35 < C153$) in agreement with experiment. An increased dipole moment of all compounds has been found in solution, induced by the external solvent field. The solvent induced red shift of the absorption energy has been reproduced both in water and acetonitrile. [5, 6]

Turning to the description of biologically relevant photoreactions, we are investigating the primary reaction in the retina protein rhodopsin (Fig. 45B) by means of unrestrained MD simulations of the full protein in a membrane mimetic environment, treating the whole chromphore at the DFT level. [8] Preliminary results from ROKS QM/MM studies suggest a mechanism, where the protein binding pocket catalyzes the reaction by steric constraints, in agreement with earlier findings from our classical MD study. [9]

For the photoactive yellow protein (PYP), the absorption spectra of a chromophore analogue, p-coumaric acid in its neutral state, have been calculated both in vacuum (Fig. 45C) and in aqueous solution, taking into account thermal fluctuations. The first peak, close to the experimentally observed absorption energy of 4.1 eV, is composed of three excited states, S_1, S_2, and S_3. The main contribution comes from S_2, which is essentially the HOMO-LUMO $\pi \rightarrow \pi^*$ transition. In the future we will extend our investigation to the study of the influence of the protonation state and of the water and protein environment on the different excited states of the PYP chromophore.

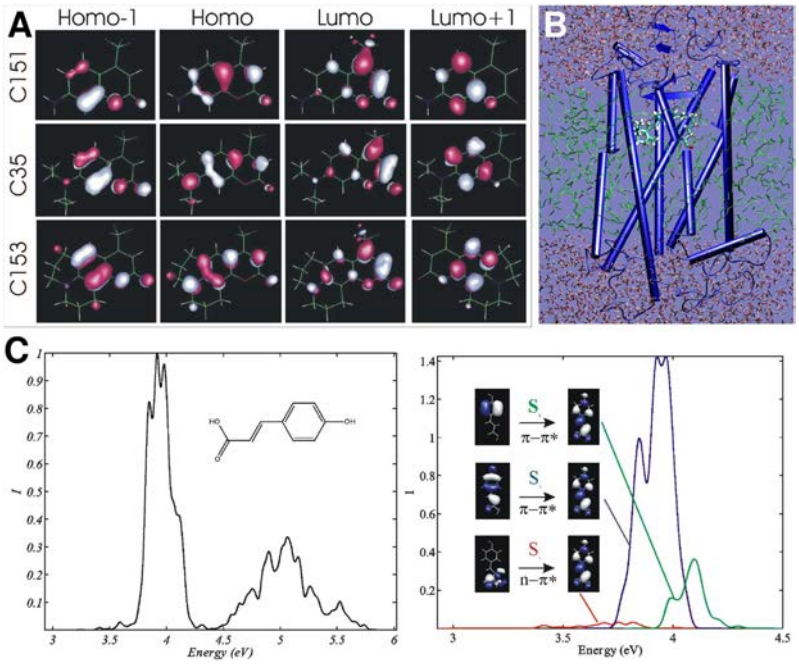

Figure 45: *A. Investigated aminocoumarin compounds (C151, C35, C153) and their chemically active orbitals from vacuum calculations. B. The rhodopsin model system: the transmembrane protein (blue) accomodates the chromophore in its center and is surrounded by the membrane (green) and an aqueous phase (red). C. Calculated absorption spectra of neutral p-coumaric acid in vacuum (left) and decomposition of the first absorption peak into its three components (right).*

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Project title: **Ab initio Hybrid Simulations of Electron Transfer Reactions**

Project leader: U. Röthlisberger

Researchers: M. Sulpizi,
I. Tavernelli

Institutions: Laboratory of Computational Chemistry and Biochemistry, EPF Lausanne

Description

We have recently introduced a novel method [1] to define dynamical electrostatic potential derived (D-RESP) charges for systems described within a Quantum Mechanics/ Molecular Mechanics (QM/MM) scheme [2]. In this part of the project we derived the analytic dependence of these charges on the quantum charge density and on the atomic positions [3]. This *variational* property can be exploited for defining interaction potentials between the quantum and the classical subsystems that depend explicitly on the value of the D-RESP charges. Such potentials can be used for a multitude of different purposes, such as improving the computational efficiency of the electrostatic coupling between the QM and the MM subsystems and for defining a QM/MM analogue of the exclusion schemes commonly used in classical biomolecular force fields. Moreover within this contest we introduced a new QM/MM based method to drive electron transfer reactions [4]. Our approach uses the D-RESP charges of the quantum atoms as a reaction coordinate and allows to estimate the free energy barrier of the electron transfer process. The meothod provides an accurate description of the electronic structure changes and of the nuclear reorganization associated with the reaction. We use the method to describe the electron-transfer induced dissociation of the m-chloro-cyano-benzene radical anion in aqueous solution [4].

Achievements

The RESP-based method has been applied to the charge driven dissociation of m-chloro-benzene radical anion [4]. The reaction is triggered by solvent reorganization. During the electron transfer process, the solvent around the nitrogen establishes an H-bond network involving on average four water molecules at difference to its equilibrium value of three. As a consequence, the negative charge on the cyano group is progressively transferred towards the benzene ring, showing an opposite trend in the charge localization with respect to the simulation with a lower value of the restrained target charge. At the onset of the reaction, charge-spin segregation is observed. The negative charge is transferred to the leaving Cl, while the spin density localizes on the non-saturated carbon atom of the benzene ring. In Fig. 46, the Kohn-Sham orbitals corresponding to the unpaired spin (HOMO) are shown as the reaction proceeds. In particular, the panel a) shows the HOMO corresponding to the bound system, in which the spin density is mostly localized on the cyano group and on the benzene ring and the orbital has π-character. In b) the HOMO at the transition state is shown, the spin density is still partially localized on the cyano group, but there is no increased density on the unsaturated carbon of the benzene ring and on the chloro substituent. Panels c) and d) show two pictures of the dissociated form: now the spin density is mostly localized on the unsaturated carbon of the benzene ring. Calculation of the free energy barrier of dissociation is performed within the umbrella sampling formalism. The obtained free energy barrier of dissociation is in good quantitative agreement with the experimental data ((12.7 $\pm$ 0.2) kcal/mol) [5, 6]. In addition, it is also possible to establish a connection with standard Marcus theory and to estimate the electronic coupling parameters for a comparison with previous calculations. The resulting value of $\sim$ 4 kcal/mol indicates a strong coupling of the two states with different charge localization, which is the expected result for electron transfer reaction which

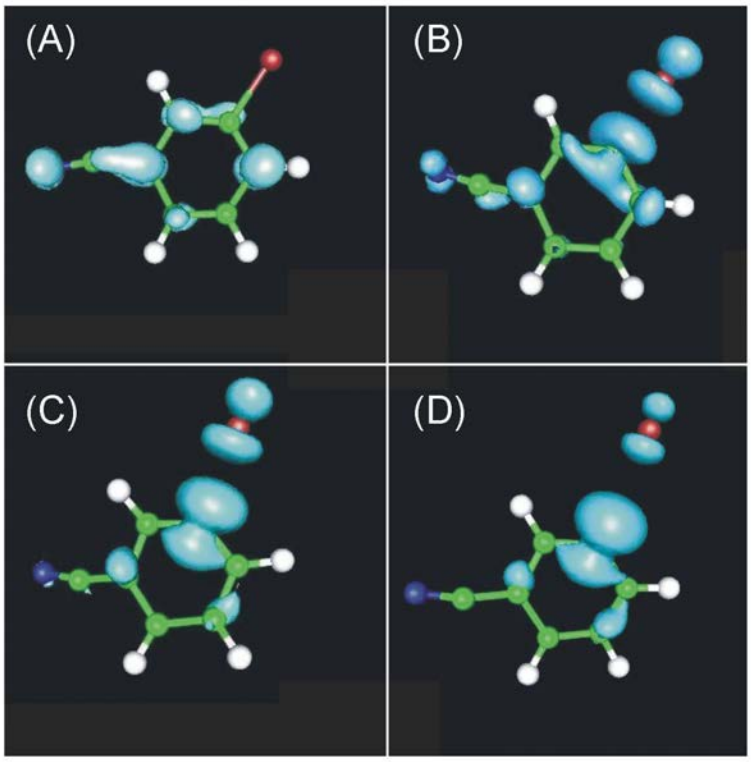

Figure 46: *Kohn-Sham orbitals corresponding to the unpaired spin (HOMO)*

involves bond breaking. Thus, our method turns out to be accurate enough to estimate the free energy barrier associated with radical anion decomposition. This type of studies can be extended to the ET description in biological systems, and can find practical applications in cases where a charge transfer is connected to a complex geometric reaction coordinate and therefore traditional thermodynamic integration is difficult to apply. We are currently extending this type of studies to electron transfer process is model peptides.

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Project title: **QM/MM simulation of the copper binding sites in mouse prion protein**

Project leader: U. Röthlisberger

Researchers: Maria Carola Colombo

Institutions: Laboratory of Computational Chemistry and Biochemistry, EPF Lausanne

Description

Prions are proteinaceous infectious agents devoid of any nucleic acid information. [1] They play a central role in a group of invariably fatal, neurodegenerative diseases affecting animals such as sheep (scrapie), cattle (bovine spongiform encephalopathy (BSE)) and humans (e.g. Creutzfeldt-Jacob disease (CJD), Gerstmann-Straussler-Scheinker syndrome, kuru and fatal familial insomnia). [2] Both the biological function of the cellular form of the prion protein and the mechanism of conversion to the pathogenic form are still largely unknown. Recently it has been demonstated that the C-terminal structured part of the prion protein is capable of binding copper ions. [3] Using pulse EPR and ENDOR spectroscopy, information was extracted about the local coordination environment of three distinct binding sites. In particular, this studies show that around neutral pH a histidine residue is involved in the coordination to the copper ion. [4] The goal of this project is to characterize the structural and chemical properties of copper-loaded prion protein starting from the experimental information.

Achievements

In this project, we perform a theoretical characterization of the structural and chemical properties of copper-containing prion proteins starting from the available NMR structure of the mouse prion protein (protein data bank code 1AG2) [5]. We have used a bioinformatics approach to localize the protein regions with the highest propensity for copper ion binding. The identified candidate structures were subsequently refined via mixed quantum-classical Car-Parrinello simulations [6] in which the area around the copper ion is treated at the gradient-corrected density functional level whereas the rest of the protein and the solvent are described via a classical biomolecular force field. Once these quantum/classical simulations were completed for all 4 putative binding sites, we performed a detailed analysis of the structural and dynamical properties. [7, 8, 9] We have also undertaken extensive calculation of the EPR properties of all sites using the Amsterdam Density Functional (ADF) software package [10] and compared the results to experimental data. The computation of EPR properties could narrow down the number of possible candidate structure to 1-2 sites (involving H177 and H187). After having extabilished the nature of the most likely copper binding sites we have now started to explore the possible biological consequences. In particulari, we have tried to answer the question of how these sites can influence the structural stability of the mouse prion protein and its transition to the scrapie form by performing irallel tempering studies of the low pH form.

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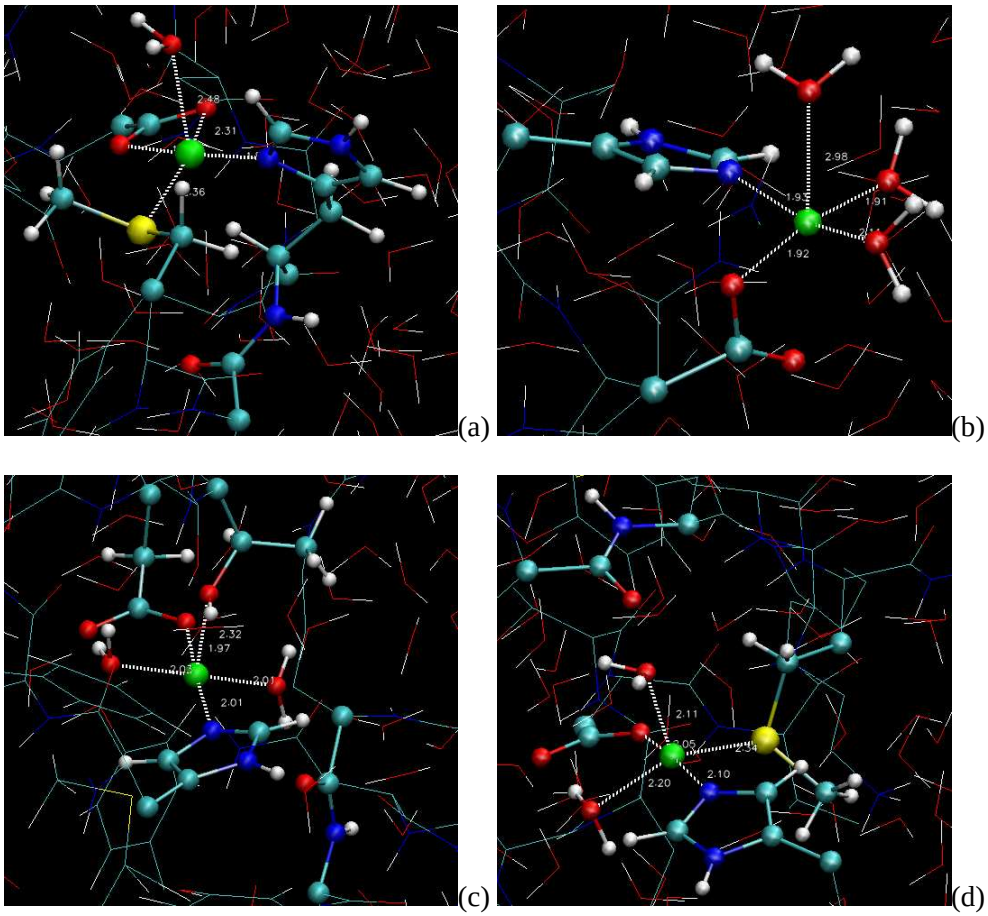

Figure 47: *Last frames of the QM/MM dynamics of the (a) H140 binding site, (b) H177 binding site, (c) H187.E binding site and (d) H187.D binding site. Atoms drawn in ball and sticks are included in the QM region, atoms in sticks are in the MM region.*

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Project title: **First-principles characterization and design of radiopharmaceuticals**

Project leader: U. Röthlisberger

Researchers: P. Maurer †

Institutions: Laboratory of Computational Chemistry and Biochemistry, EPF Lausanne
† Inorganic Chemistry, ETH Zürich

Description

Radiopharmaceuticals are drugs containing a radioactive nucleus. A key goal in radiopharmaceutical research is the development of anticancer drugs which deliver a radioactive nucleus selectively to cancerous tissue. Thus, the source of radiation is located *inside* the tumor, which should lead to a more effective treatment with less side-effects compared to conventional radiotherapy with an external source.

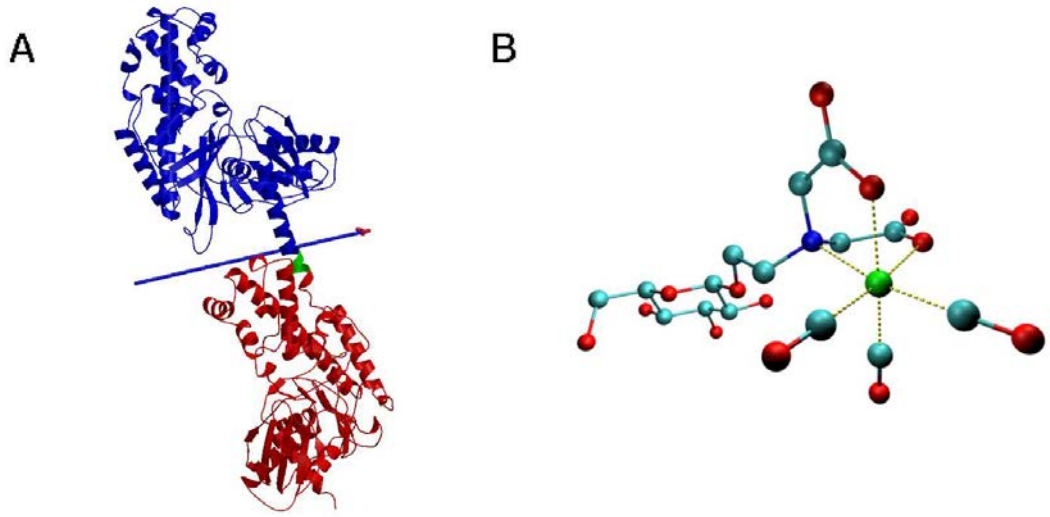

Figure 48: ***A:*** *Cartoon representation of human hexokinase-I. The N-terminal half is shown in* blue*, the C-terminal half in* red*. A principal components analysis (PCA) shows that the dominant motion is a bending motion of the N- and C-terminal halves relative to each other. The bending residues are indicated in* green*, the* blue arrow *indicates the position of the bending axis.* ***B:*** *Glucose is functionalized with an IDA chelating moiety at the C-2 position. The resulting complex with the* $[Tc(CO)_3]^+$ *core is sufficiently stable in human serum for application as a radiopharmaceutical.*

High glycolytic activity is a well known feature of many malignant, fast growing, tumors. The enzyme hexokinase-I (Fig.48A), which catalyzes the first step of glycolysis (the phosphorylation of glucose to produce glucose-6-phosphate), is therefore a promising target for both diagnostic and therapeutic radiopharmaceutical agents. Hexokinase-I is a 100 kDa enzyme and consists of two highly similar halves, each of which contains a binding site for glucose. As a part of this project, we have performed 8 ns of classical molecular dynamics simulation of human hexokinase-I in

explicit aqueous solution (180'000 atoms in total) [3]. This simulation gives new insight into domain motions and suggests a reinterpretation of the differences which are observed in experimental crystal structures. A simulation of a truncated C-terminal half ("mini-hexokinase") shows only minimal structural differences compared to the complete enzyme. Thus, it will be sufficient to include only the C-terminal half in future investigations of the interaction of radioactively labelled glucose with hexokinase, which allows for considerable savings in the required computer time.
Glucose has recently been successfully labelled with ^{99m}Tc in Prof. Schubiger's group (PSI/ETHZ), via functionalization of glucose with an imino-diacetic acid (IDA) chelator at the C-2 position (Fig.48B). A crystal structure of this compound is however not available so far. We have performed QM and QM/MM calculations in order to provide a structural characterization of this compound in gas phase and in aqueous solution [4]. Future work within this project will involve the investigation of the binding of labelled glucose to hexokinase in order to support experimentalists in their search for compounds with stronger binding affinities.

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Project title: **QM/MM hybrid Car-Parrinello simulations of the catalytic mechanisms of DNA repair enzymes**

Project leader: U. Röthlisberger

Researchers: Denis Bucher,
Håkan W. Hugosson.

Institutions: Laboratory of Computational Chemistry and Biochemistry, EPF Lausanne

Description

The genetic information encoded in the DNA is protected by a sophisticated control system involving the concerted action of several repair enzymes that can spot specific DNA damages and correct them back to the original state. [1] The major defense strategy against DNA base damage such as deamination, oxidation, or alkylation reactions, is the base excision repair (BER) pathway. [2] BER involves cleavage of the aberrant base from the DNA backbone and leads to an abasic site which is highly mutagenic and has to be removed rapidly. In recent years, high-resolution crystal structures of several enzymes involved in DNA repair have become available, including complexes with substrate analogues and intermediates in various states of repair. [3]
The aim of this project is to perform first-principles QM/MM simulations of the catalytic mechanism of the prototypical DNA repair enzyme Endonuclease IV (Endo IV) (fig. 49A), thereby contributing to the fundamental understanding of the catalytic mechanism, identifying the relevant key factors that influence the catalytic activity, and providing a mechanistic basis for the development of strategies for therapeutic interventions.
In order to address these challenging systems, and to determine the ability of our theoretical tools to describe them, we have, together with other projects studying nucleic acid systems, [4] carried out comparative theoretical studies of nucleotide and nucleoside solvation (the building blocks of nucleic acids) in water. [11] In these molecular dynamics simulations we use a range of theoretical methods, from purely classical force field simulations (AMBER), [5] via a hybrid QM/MM scheme, [6, 7, 8] to fully quantum mechanical calculations, within the Car-Parrinello [9] molecular dynamics (using the CPMD program [10]). The quality of the classical force field can be assessed and, where necessary, reparameterized in a direct force-matching procedure.

Achievements

Classical, QM/MM, and full QM simulations have been performed, on the RNA and DNA forms of adenine and adenosine. The simulations have been analysed, e.g. investigating solvation patterns around the nucleic base, phosphate group and sugar ring, sugar ring puckering (pseudorotation), and the description of the electrostatics (e.g. the dipole moments given by D-RESP fitted point charges [7]).
In summary, we find that both the classical force field and the QM/MM simulations agree well with full QM simulations of the solvation patterns, justifying the use of these two methods in the description of nucleic acid systems.
Classical equilibration of the structure of the DNA repair enzyme Endonuclease IV has been performed, and the first steps in the QM/MM treatment of the system are also in progress.

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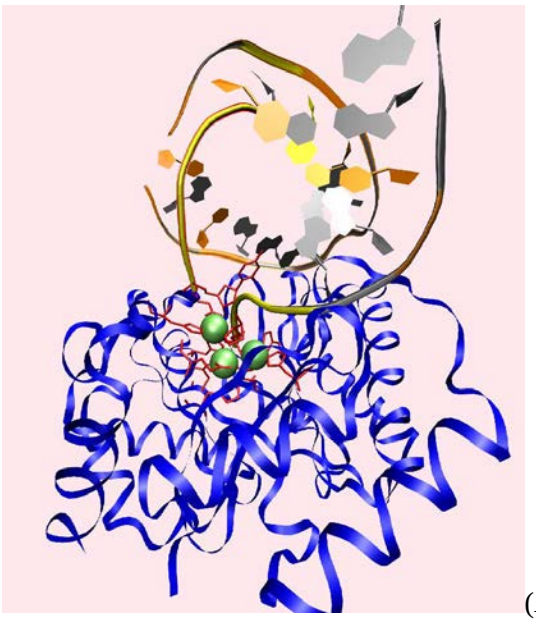
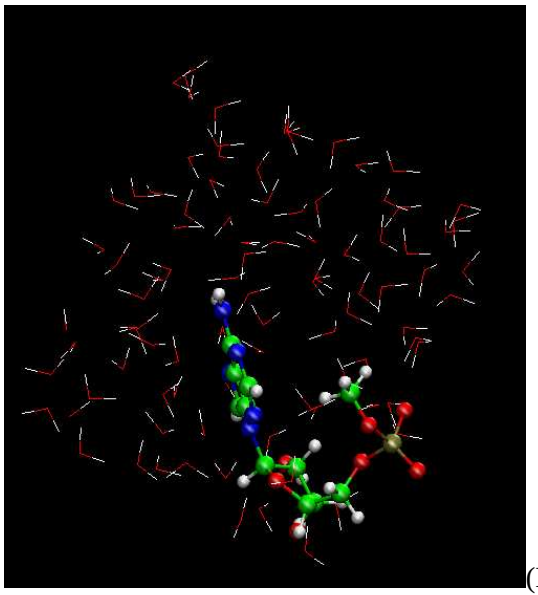

(A)

(B)

Figure 49: **(A)** *The DNA repair enzyme Endonuclease IV (Endo IV).* **(B)** *A typical test case: RNA adenine solvated in water.*

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Project title: **Formation and Evolution of the Milky Way**

Project leader: M. Samland

Researchers: A. Immeli

Institutions: Astronomical Institute, University of Basel

Description

In this project we investigate how disk galaxies form inside growing dark matter halos in a realistic ΛCDM cosmogony. This is one of the important unsolved problems in astrophysics today. The formation and evolution of a galaxy is influenced by the cosmological initial conditions and the environment, but also by internal feedback processes. Heating by supernovae (SNe), dissipation, radiative cooling, as well as in- and outflows influence the evolution of galaxies both locally and globally.
We developed a three-dimensional computer program, to simulate the dynamics of dark matter, stars, and the multi-phase interstellar medium, as well as the interaction processes which connect dark matter, stars, and gas phases. The simulations provide new insights into the details of the galaxy formation processes and cosmological evolution in general. In addition, star formation rates, colours and sizes of the modeled galaxies can be used to analyse high redshift objects (galaxies in the early universe). The goal of the project is a self-consistent evolution model for the Milky Way and similar galaxies, which will be important for several research fields in astrophysics.

The numerical method:

We use particle-mesh codes to follow the dynamical evolution of the collision-less systems of stars and dark matter. For the dynamical description of the interstellar medium (hot, warm and cold gas phases) we use three-dimensional hydrodynamical grid codes. The dark and baryonic components are coupled by gravitational forces. The mass, momentum and energy exchange processes between the stars and the interstellar medium are described with an interaction network. The network, includes star formation, stellar mass return, heating and cooling by radiation, dissipation, formation and evaporation of cold clouds in the hot intercloud medium and the nucleosynthesis([4, 10, 11]).

A Milky Way Model:

In the following we give a brief description of our new Milky Way formation model. The simulation starts at a redshift of $z = 5$ with a small dark halo of 2.1×10^{10} solar mass. Inside the growing dark halo a disk galaxy forms, whose star formation rate reaches a maximum of 50 solar mass per year at redshift $z \approx 1$. The galaxy forms radially from inside-out and vertically from halo to disk. The first galactic component that forms is the halo, followed by the bulge, the disk-halo transition region, and the disk. At redshift $z \approx 1$, a bar begins to form which later turns into a triaxial bulge. Despite the still idealized model, the final galaxy resembles present-day Milky Way in many aspects (Fig. 50). The bulge in the model consists of at least two stellar subpopulations, an early collapse population and a population that formed later in the bar. The initial metallicity gradients in the disk are later smoothed out by large scale gas motions induced by the bar. There is a pronounced deficiency of low-metallicity disk stars due to pre-enrichment of the disk interstellar medium with metal-rich gas from the bulge and inner disk (”G-dwarf problem”). The mean rotation and the distribution of orbital eccentricities for all stars as a function of metallicity are not very different from those observed in the solar neighbourhood, showing that early homogeneous

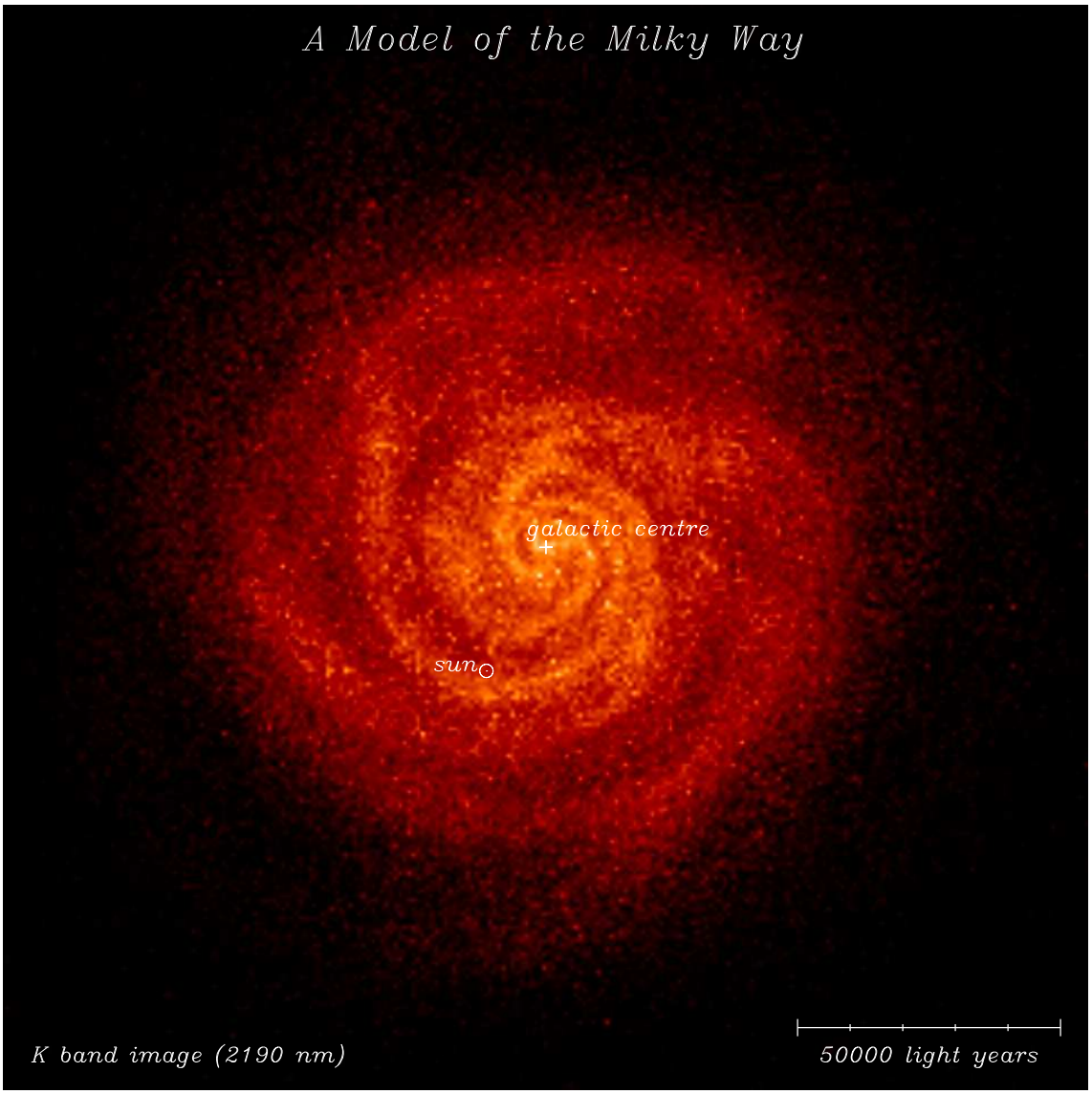

Figure 50: *Surface brightness of a Milky Way model in the K band.*

collapse models are oversimplified. The present approach provides a detailed description of the formation and evolution of an isolated disk galaxy in a ΛCDM universe, yielding new information about the kinematical and chemical history of the stars and the interstellar medium ([4, 5, 1]).

Galaxies in the Early Universe:

The present chemo-dynamical model provides kinematics and metallicities of individual stars, but also can be used to obtain colours, metallicities and velocity dispersions of integrated stellar populations. It therefore can be used as a tool to understand observations of distant spiral galaxies, and connect them with stellar data in the Milky Way. In addition, it provides gas phase metallicities and temperatures, and star formation rates, as a function of time or redshift. We have already used this information to predict the colour evolution of large spiral galaxies, and have it compared with

bulge colours in the Hubble Deep Field ([6, 9, 4, 1]).

Gas Physics and Disk Fragmentation:

In a sub-project we have investigated the evolution of star-forming gas-rich disks. We could show that galaxy evolution proceeds along very different routes depending on whether it is the gas disk or the stellar disk which first becomes unstable. This in turn depends on the uncertain efficiency of energy dissipation of the cold cloud component from which stars form. When the cold gas cools efficiently and drives the instability, the galactic disk fragments and forms a number of massive clumps of stars and gas. The clumps spiral to the centre of the galaxy in a few dynamical times and merge there to form a central bulge component in a strong starburst. When the kinetic energy of the cold clouds is dissipated at a lower rate, stars form from the gas in a more quiescent mode, and an instability only sets in at later times, when the surface density of the stellar disk has grown sufficiently high. The system then forms a stellar bar, which channels gas into the centre, evolves and forms a bulge whose stars are the result of a more extended star formation history ([2, 3, 8]).

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Project title: **Modelling Weather and Climate on European and Alpine Scales**

Project leader: C. Schär

Researchers: P.L Vidale
D. Lüthi
C. Frei

Institutions: Institute for Atmospheric and Climate Science, ETH Zürich

Description

Our research revolves around the study of continental and Alpine-scale weather and climate, with special focus on the water cycle, over a continuum of spatial and temporal scales. Regional climate processes are investigated with the help of a regional climate model (RCM), the Climate High-Resolution Model (CHRM). The dynamics of dry and moist atmospheric flow past realistic and idealized topography are investigated with the help of a hierarchy of hydrostatic and non-hydrostatic atmospheric models (e.g. MC2, HRM, ARPS, LM). Hydrological processes in intermediate and major catchments in the Alpine region are investigated with the help of hydrological models (e.g. with WASIM).

Climate-related studies

Research on climate aspects is dedicated to the study of natural and anthropogenic climate variations on seasonal to centennial time scales. Our research revolves around the study of continental and Alpine-scale weather and climate, with special focus on the water cycle, over a continuum of spatial and temporal scales. This work involves conducting comprehensive RCM numerical simulations at horizontal resolutions between 14 and 56 km, driven by the output of intermediate-resolution general circulation models and reanalysis data sets. For the simulation of European regional climate, multiple state of the art, general circulation models (GCMs) are currently run at high resolution (grid spacing equivalent down to 100 km) by the European climate community in the context of two major research projects which will be active for the next few years, one funded by the Swiss SNF (NCCR Climate), the other by the European Commission (PRUDENCE). These current and future (scenario) simulations, together with the re-analyses provided by the European Center for Middle-Range Weather Forecasts (ECMWF, ERA-15 and ERA-40) are used to drive RCMs, which serve as dynamical downscaling tools. Our own CHRM, which we have extensively applied and verified in the past (using ERA-15 forcing data), is forced at the boundaries (nudged) with global data provided by the Hadley Center (HadAM3h) and the Max Planck Institut (ECHAM) GCMs. These simulations, with Δx of 56 and 14 km, use a nested grid approach and cover a 30 year period under current climate conditions in addition to a 2071-2100 period, driven by climate change scenarios (e.g. SRES A2, B2). Results of the 56 Km simulations stored at our Institute are accessed by many European PRUDENCE partners, through OpenDAP technology, and used for impacts modeling. The 14 km simulations are used to drive the WASIM hydrological model ([1]), also for impacts studies.The principal focus of the PRUDENCE project is the production of regional climate change information, and the assessment of its reliability (as related to climate) but also of the dependence on different model formulations. Estimate of local impacts and risks are also produced in this context. The NCCR Climate project has broader scientific focus, but also covers continental climate processes, such as the moisture cycle (and relative feedbacks) within the soil, the land surface and the atmosphere. Our contribution to the NCCR Climate project also concurrently addresses research topics related to the debate on the ability of the GCMs to credibly represent tropospheric moisture dynamics and thermodynamics

within different scenarios, together with consequences for precipitation estimation over the North Atlantic-European domain.

Weather-related studies
Research on weather aspects is motivated by the emergence of high-resolution cloud-resolving models. Such models offer promising prospects in numerical weather prediction as well as quantitative precipitation and flood forecasting. In the context of modeling of high-resolution Alpine weather, most of the activities in the past year consisted in work with a convection-resolving numerical model. During the field phase (September 7 - November 15, 1999) of the Mesoscale Alpine Programme (MAP), the MC2 model has been run at CSCS in real-time with a horizontal resolution of 3 km, and a computational domain of 350x300x50 grid points covering the whole of the Alpine region. The purpose of the Mesoscale Alpine Project (MAP) is to improve the understanding of orographically influenced precipitation events and related flooding episodes involving deep convection, frontal precipitation and runoff. This includes the numerical prediction of moist processes over and in the vicinity of complex topography; the understanding and forecasting of the life-cycle of Foehn-related phenomena; the study of three-dimensional gravity wave breaking and associated wave drag; and the production of data sets for the validation and improvement of high-resolution numerical weather prediction, hydrological and coupled models in mountainous terrain. These research goals are pursued by exercising a hierarchy of numerical models, also applied in weather forecasting, and applying them at very high resolution to case studied of relevant weather events, which were amply documented by the MAP datasets.

Achievements
Previous work had focused on the validation of our RCM, the IAC-ETH CHRM ([2], [3]), driven by ECMWF re-analysis data, focusing on interannual variability and process studies. Joint papers with European partners have also addressed the ability of the CHRM model to represent precipitation at the daily time scale over a recent climatic period ([4]) and the soundness of physical processes at the land surface ([5]).In the last year we have reached one important milestone in our regional climate modeling (RCM) capabilities, with the completion of the first set of simulations driven at the lateral boundaries by a state of the art GCM, the Hadley Center HadAM3, as part of our work in the PRUDENCE project. These current and future (scenario) simulations, together with the re-analyses provided by the European Center for Middle-Range Weather Forecasts (ECMWF, ERA-15 and ERA-40) are used to drive RCMs, which serve as dynamical downscaling tools. The CHRM simulations, with Δx of 56 and 14 km, use a nested grid approach and cover a 30 year period under current climate conditions in addition to a 2071-2100 period, driven by SRES A2 climate change scenarios. The results of these experiments have been used in-house for the production of statistical products, investigating changes in drought/heat wave persistence, or changes in high precipitation intensity distribution (e.g. [4]). In addition, results are analyzed with regard to process studies (e.g. [6]). The results have also been made available to the entire European impacts modeling community through OpenDAP technology (WWW-based data distribution), so that CHRM output fields are used to drive a hierarchy of hydrology, agriculture, storm surge and even socio-economic models.
A very important result in terms of public outreach has been achieved through publication of our scenario integrations results in the context of understanding physical mechanisms involved in exceptionally warm and dry European summers, which were recently published in a Nature [7] paper. This publication spawned a large amount of media queries and interviews (TV, radio) at both national and international level.
During the last year, a PhD thesis on predictability has been completed (see [8], [9]). We investi-

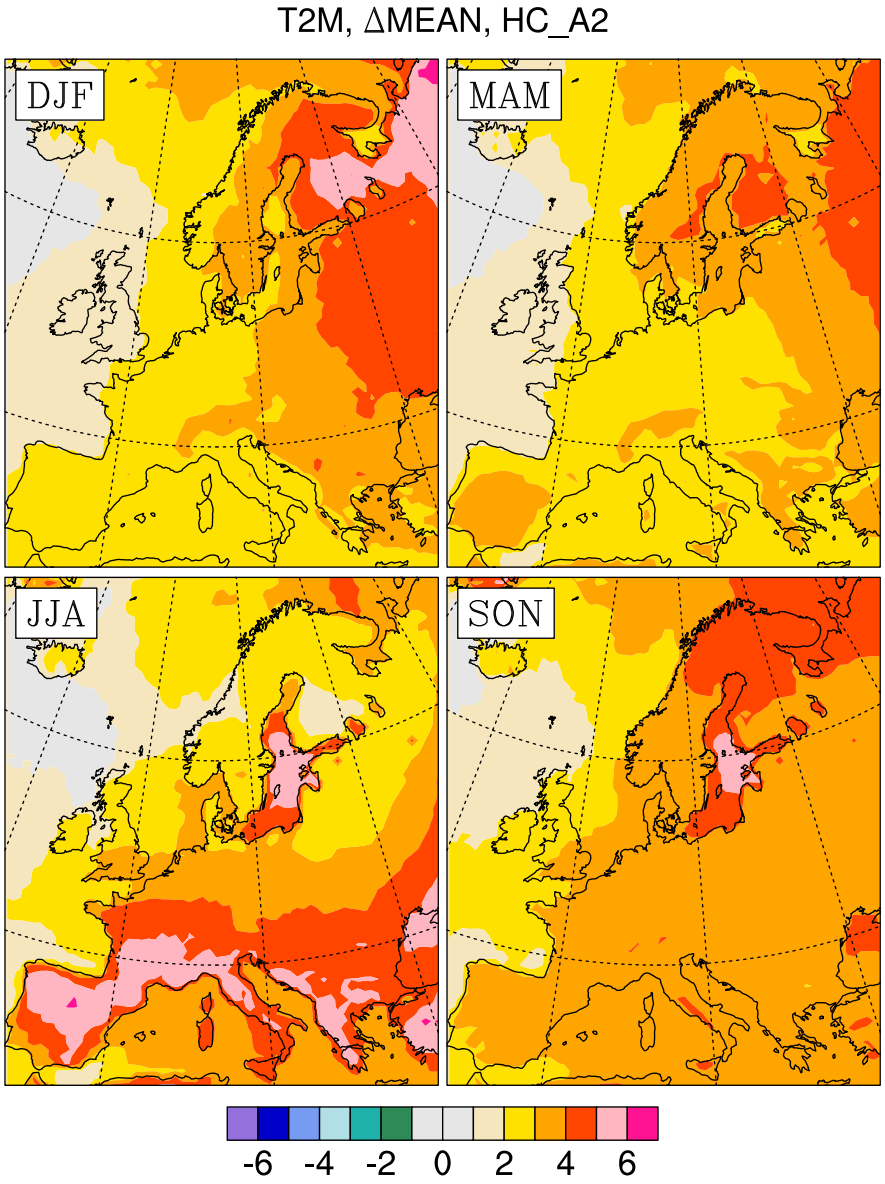

Figure 51: *An example of CHRM results: seasonal temperature change for the 2071-2100 under an A2 scenario (period 1961-1990 is reference)*

gate how explicit dynamics implies predictability limitations, in particular regarding the prediction of heavy precipitation events. This work is being continued by a new PhD thesis of Cathy Ho-

henegger. (see below). In addition, a detailed observational / numerical study has been completed that addresses the structure of the Alpine wake ([10], [11]). Work on the formulation of vertical coordinate formulation ([12], [13]) has continued. Our proposal to use smooth coordinate surfaces has been met with substantial interest, and the new coordinate formulation has successfully been implemented in several major mesoscale models by other research groups (among them the Meso-NH of MeteoFrance, the LM of the German Weather Service and MeteoSwiss, and the MM5 of NCAR). On the idealized mesoscale modeling side, we have shifted the focus of our numerical modelling work to the Advanced Regional Prediction System (ARPS). The model has been compiled and optimized on the NEC-SX/5 platform and a good level of performance has been achieved. Research using ARPS has focused on idealized flow past topographic obstacles ([14]). The results of these experiments have helped to further our understanding of the properties of moist embedded convection and potential vorticity generation in flow past mountain barriers.

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Project title: **Variability of the Sun and Global Climate**

Project leader: W. Schmutz[1]

Researchers: T. Egorova[1,2]
M. Haberreiter[1,3]
E. Rozanov[1,2]
M. Schraner[2]
T. Wenzler[3]
M. Wild[2]

Institutions: [1]PMOD/WRC (Physikalisch-Meteorologisches Observatorium/World Radiation Center), Davos
[2]IAC (Institute for Climate and Atmospheric Sciences), ETH Zürich
[3]IfA (Institute for Astronomy), ETH Zürich

Description

The goal of the project is to understand how the Earth's climate responds to the variations of the solar activity. We investigate the effect of variations of the solar irradiance, in particular the spectral variability with emphasis on the UV radiation, on ozone and other trace gases, and we evaluate their influence on the dynamics and temperature of the atmosphere, from the mesopause down to the Earth's surface. The investigation includes several steady-state and transient numerical experiments with a newly developed state-of-the-art global climate-chemistry model SOCOL to study the sensitivity of the ozone and climate to the variability of the solar spectral irradiance and to estimate the solar signal in ozone and climate during the last two decades (1975-2000). The transient experiments require the knowledge of the monthly mean spectral distribution of the solar irradiance for 1975-1991, which has not been measured and therefore, has to be calculated in the project's framework. According to the research plan the entire project is divided into four subprojects: (i) understanding the total solar irradiance variability on the basis of magnetic field strength analysis; (ii) calculations of the solar UV irradiance for the past and present; (iii) development of the general circulation model with interactive chemistry and sensitivity studies with the model; and (iv) study of the transient climate and chemistry responses to the variability of the solar forcing.

Achievements

Using CSCS and our own facilities we have performed two 20-year long steady-state simulations for solar max and min cases with previously developed Chemistry-Climate model SOCOL. The solar signal in the zonal mean annual mean temperature and ozone is obtained as a difference between solar max and solar min cases. For the temperature we obtained statistically significant warming in most of the stratosphere by up to 1.2K at the stratopause in the tropics and up to 1.5K over the high-latitudes. In the mesosphere the solar signal in the temperature field is also positive due to the enhancement of the solar irradiance and reaches up to 2K over southern high latitudes in the lower mesosphere and up to 1.8K in the tropical upper mesosphere. A well pronounced dipole vertical structure over the poles is a result of polar night jet (PNJ) acceleration. For the ozone changes we have obtained an increase of ozone up to 2.5% in the stratosphere due to an intensification of the oxygen photolysis and ozone decrease in the mesosphere (65-75 km) that occurs mainly due to elevated HO_x production from the enhanced H_2O photolysis in the Lyman-α line. These results can be qualified as theoretically expected. Our results also reveal a statistically significant warming of the annual mean surface air by up to 1K over North America and 1.2K

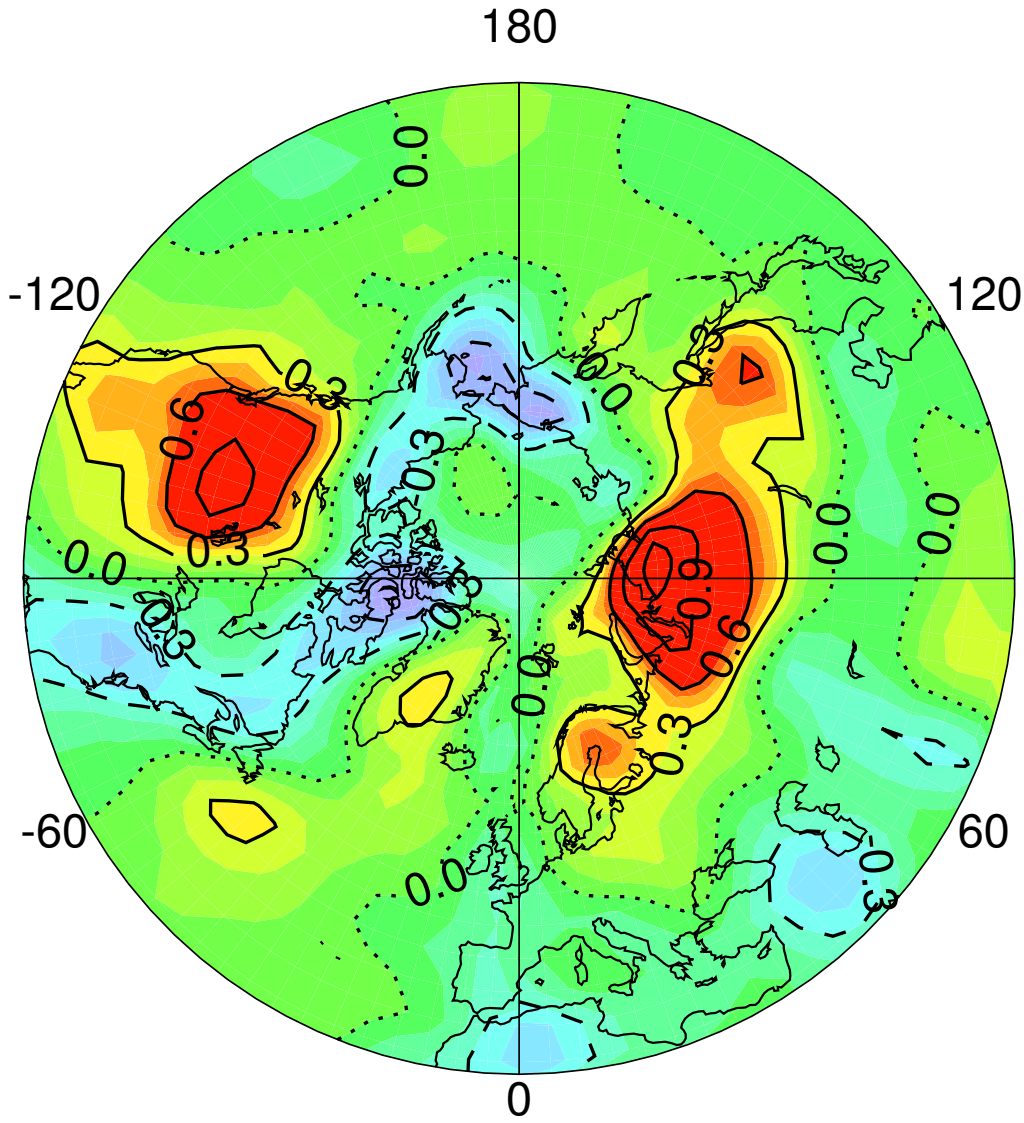

Figure 52: *Annual mean solar signal in surface air temperature for the Northern Hemisphere.*

over Siberia (see Fig. 52). The pattern of the temperature response resembles the changes between positive and negative Arctic Oscillation phases, which implies downward propagation of the solar signal via intensification of the PNJ. These results are presented by Egorova et al. (2004). The other results of the project are presented in the papers listed below.

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Project title: **MONALISA: Modelling and Reconstruction of North Atlantic Climate System Variability**

Project leader: T. F. Stocker

Researchers: C. C. Raible
M. Yoshimori
M. Renold
U. Beyerle

Institutions: Climate and Environmental Physics, Physics Institute, University of Bern

Description

MONALISA[15] is one of 13 projects in the NCCR-Climate (National Centre for Competence in Research - Climate)[16]. The goal of this project is to understand mechanisms responsible for natural climate variability on decadal to centennial time scales. The emphasis is placed on the North Atlantic and European regions. We use the comprehensive climate model, CCSM (Community Climate System Model), from NCAR (National Center of Atmospheric Research, Boulder, CO, USA) to simulate the present climate and the climate over the last 500 years. For the latter simulation, past solar activity, volcanic eruptions, and greenhouse gas concentrations (e.g., carbon dioxide) are taken into account.

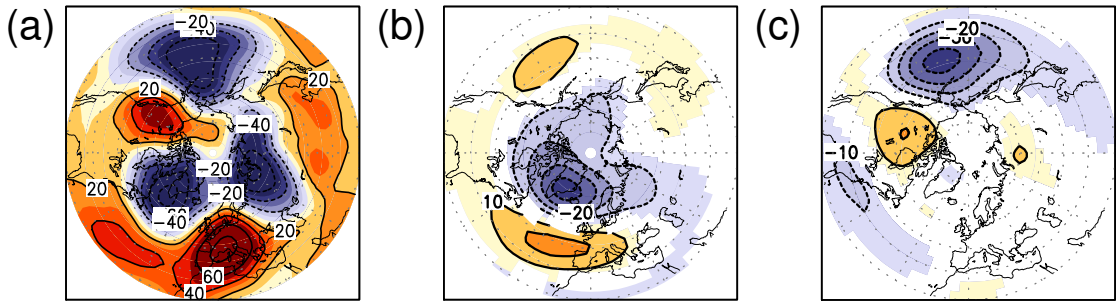

Figure 53: *Observed (a) and mean simulated (b, c) 50-yr trend patterns of the 500 hPa geopotential height (0°N to 87°N) averaged over both model simulations (ECHO-G and CCSM) for winter (DJF). For the model simulations composites are estimated where the NAO 50-yr trends exceed more than one standard deviation (b) and where the AL 50-yr trends exceed minus one standard deviation (c). Shading indicates values which are significant at the 99% level (b, c). The contour increment is 10 gpm per 50 yrs (from Raible et al., 2004).*

Achievements

In the first part of the project, we investigated decadal trends of the Northern Hemisphere atmospheric circulation in winter [1]. The observed 500 hPa geopotential height trend pattern of the last 50 years (Fig. 53 a) shows a strong North Atlantic Oscillation (NAO) trend toward its positive phase whereas the Aleutian Low (AL) exhibits a negative trend. The comparison with reconstructions of the past 500 years and model simulations suggests that this simultaneous appearance of

[15] http://www.climate.unibe.ch/∼raible/nccr/start_p11_intro.html
[16] http://www.nccr-climate.unibe.ch

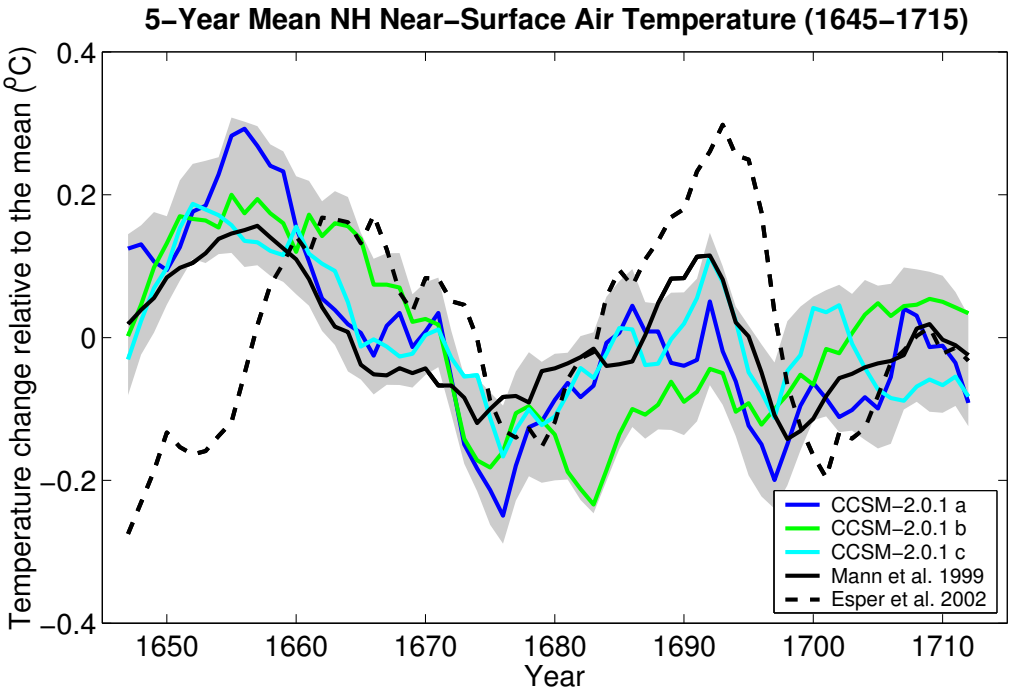

Figure 54: *Comparison of Northern Hemisphere mean temperature changes between model simulations (ensemble members: a, b, and c) and two proxy-based reconstructions during the Maunder Minimum. Temperature changes are expressed as departures from the mean of each time series. The shading represents +/– one standard deviation of ensemble members from the ensemble mean.*

trends in the Northern Hemisphere is a rather rare event. The composite of multi-model simulations for strong positive NAO trends indicate a weak positive trend nearby the Aleutian Islands (Fig. 53 b); for strong negative AL trends the North Atlantic region exhibit no significant trends. Moreover, the multi-model simulations show that strong positive winter NAO trends are connected with the tripole sea surface temperature (SST) pattern and a northward shift of the storm track tail. Strong negative winter trends of the Aleutian Low go along with SST warming in the El Niño-Southern Oscillation region and a westward shift of rainfall in the Pacific. The findings suggest that the positive winter NAO trend of the last 50 years is not statistically different from internal atmosphere-ocean variability. However, the simultaneous strong negative trend of the Aleutian Low, which is triggered partly by the tropical Pacific, is possibly influenced by external forcing, e.g., global warming, volcanism, and/or solar activity change.

In the second part of the project, we investigate the variability of European climate in the historical past. One of the distinct cold periods over large parts of Europe spans the late 17th to early 18th centuries and corresponds to the period of persistent reduced solar activity, the so-called Maunder Minimum. Concurrent volcanic eruptions and the presence of internal climate variability complicate cause and effect. We conducted an ensemble simulation starting from three different initial conditions but under the same time-varying solar and volcanic forcing for this period [3]. Despite uncertainties in the past forcing, the simulated hemispheric temperature on decadal time scales agrees well with one paleoclimatic reconstruction primarily based on tree rings [4] (Fig. 54). Agreement with an alternative reconstruction [5] is weaker suggesting that the amplitude of

decadal variability might be overestimated in that reconstruction.
The spatial patterns of extreme and mean of warm and cold winters are also captured by the model although their magnitudes are overestimated (not shown). As reconstructions are limited in the number of variables and the spatial coverage, the model helps interpret the underlying mechanisms. The investigation of various fields and other parts of the world not covered by the reconstruction, confirms that both extreme and composite patterns are associated with the NAO. Further investigations with respect to the volcano-climate link and the effect of uncertainties in the forcing are in progress. Technically, the major achievement was to port the CCSM model code to our local Linux cluster platform. This gave us the possibility to integrate the model for short time windows (up to 100 model years is possible in a reasonable time) and to do model development. As a contribution to the CCSM community technical details with respect to the model adaptation to the Linux environment was given to the Software Engineering Working Group of the NCAR and is also made open to the public[17] [6].

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Project title: **Modeling of Nanostructured Materials**

Project leader: H. Van Swygenhoven

Researchers: P. M. Derlet
A. Hasnaoui

Institutions: Paul Scherrer Institute, Computer Modelling and Experiment, ASQ/NUM

Description

The deformation behaviour of nc materials is characterized by features that are different from those of their coarse-grained counterparts. The nature of these deviations remains a subject of controversy. For grain sizes below 20nm, simulation suggests that grain boundary sliding is a dominant deformation mechanism, and that cooperative grain activity may also occur. Such co-operative activity may be driven by the need to overcome grain boundary obstacles, where two or more grain boundaries must cooperate to form a plane interface, which then by further interconnection with other plane interfaces, will lead to long-range sliding [1]. Additionally, special grain boundary misorientations that are unable to accommodate grain boundary sliding easily, might form the nucleus of a cluster of grains that slide collectively [2].

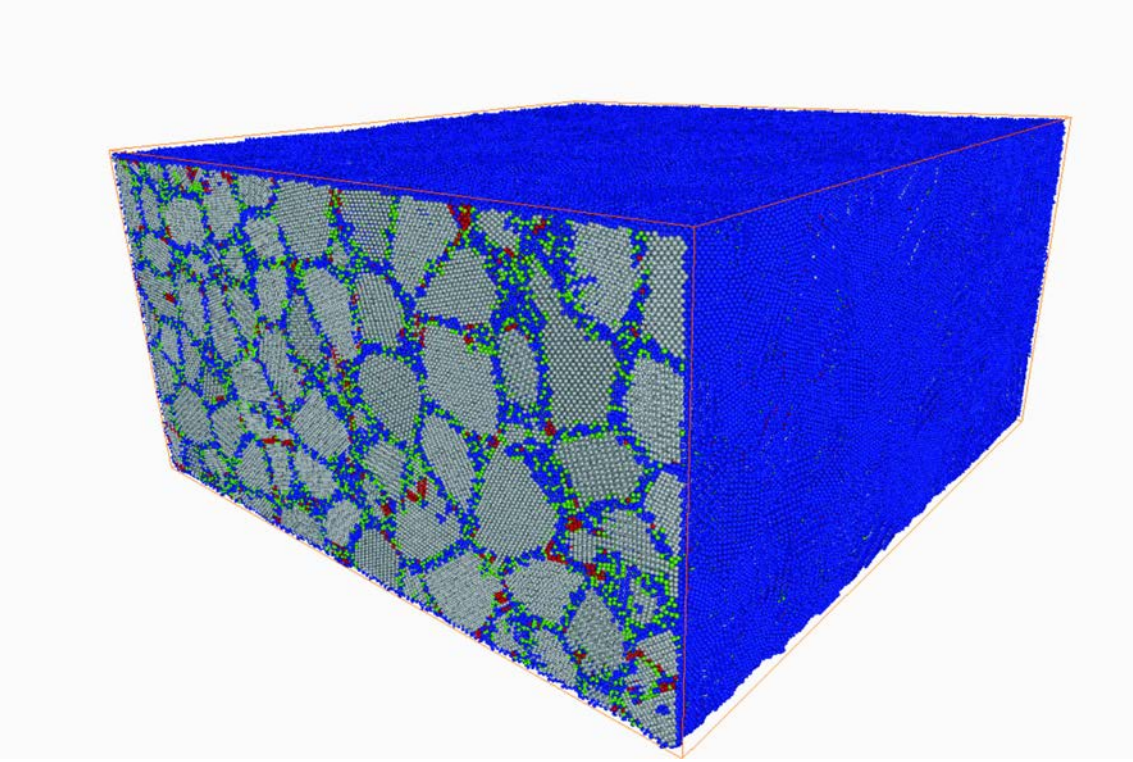

Figure 55: *Computer generated nc sample containing 750 fcc grains with an average diameter of 5nm*

To study such effects, large scale molecular dynamics simulations are used to simulate the plastic deformation of a nanocrystalline model Ni sample containing 750 grains with an average grain size of 5nm. Such large grain numbers are required to facilitate long range collective grain deformation. Fig. 55 displays the entire sample, where each atom is coloured according to their local crystalline

symmetry: grey represents fcc atoms, red hcp atoms, green other 12-coordinated atoms, and blue non-12-coordinated atoms. The deformation simulations are performed in which the sample is loaded under an applied uniaxial tension with transverse open boundary conditions and a periodic boundary condition along the tensile direction. Such geometry simulates a free standing nano-beam - in fig. 55 the blue outer layer of less than 12 coordinate atoms indicate the surface region.

Achievements

In such simulations emerging shear planes involving several grain boundaries have been observed indicating cooperative plastic deformation activity between grains. It is found that three mechanisms have been involved in the development of such shear planes: grain boundary migration, continuity of shear plane via intragranular slip, and rotation and coalescence of grains. Under the free standing beam geometry it now becomes possible to investigate whether or not shear planes resulting from cooperative grain activity can span the entire gauge of the nano-beam and thus significantly contribute to the observed plastic strain. Such grain activity requires significant atomic activity and long simulation times are required to begin to overcome the time restrictions of the molecular dynamics technique. At the present 0.5 nsec timescale, atomic visualisation indicates that surface inhomogeneities involving many grains do form along the maximum resolved shear stress directions (45 degrees to the tensile axis) and that these might indeed correspond to the early stages of long range shear plane formation.

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Project title: **Computational Quantum Chemistry of Increasingly Complex Systems**

Project leader: *Jacques Weber*,
Pierre-Yves Morgantini,
Tomasz Adam Wesolowski

Researchers: Delphine Bas,
Clemence Corminboeuf,
Marcin Dulak,
Pierre-Yves Morgantini,
Fabien Tran,
Jacques Weber,
Tomasz A. Wesolowski

Institutions: Department of Physical Chemistry, University of Geneva

Description

The computer resources at CSCS in Manno increased significantly the pool of computers available to our group. As a result, some of the sub-projects studied in our lab could be accomplished faster. They are listed below.

Achievements

A) One of the aims of the computer modelling studies of [4]heterohelicenium cation, a large organic chiral molecule (see Figure 56) was the determination of the enantiomeric form (denoted as either M or P) occurring in experimental conditions. This was achieved by comparing the theoretical Vibrational Circular Dichroism (VCD) spectra with the measured ones. Due to the fact that the theoretical rotation strengths of the two enantiomers have opposite signs, comparison between the theoretical and experimental VCD spectra allows one to identify the enantiomer occurring in the experimental conditions in a straightforward manner (see Figure 56).

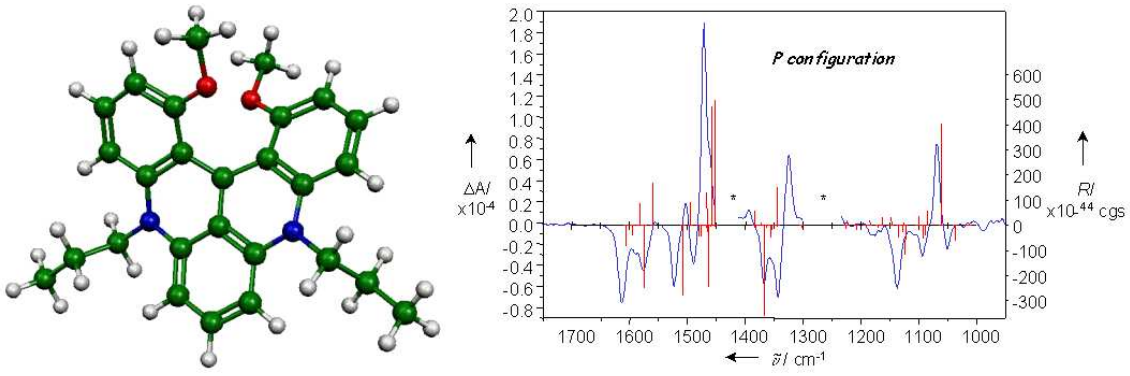

Figure 56: *The P-enantiomer of the [4]heterohelicenium molecule and the corresponding theoretical VCD spectrum. The experimental VCD spectrum is given for comparison.*

B) The computer modelling studies of King's sultam were aimed at determination which of its possible conformers (axial or equatorial) occurs in liquid phase. IR and Raman spectra measured

of sultam in either solid and in various liquids were analyzed in terms of calculated gas-phase spectra [2].

C) The computer modelling studies of the complexes formed by dibenzo-18-crown-6 (DB18C6) and water provided an useful source of complementary information concerning the properties of such complexes emerging from experimental measurements [3]. In particular: *i*) The position and orientation of the water molecule trapped inside a channel formed by stacked DB18C6 have been determined. *ii*) Most of the IR and Raman bands measured for DB18C6 in varius solvents and in the solid phase have been assigned. *iii*) The effect of the protonation of the water on the structural and vibrational properties of DB18C6 was analyzed.

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Project title: **Modelling complex molecular systems using embedded cluster approach**

Project leader: T.A. Wesolowski

Researchers: T.A. Wesolowski,
D. Bas,
M. Dulak,
F. Tran

Institutions: Department of Physical Chemistry, University of Geneva

Description

The computer simulations performed at CSCS in Manno, form an integral part of our long standing interest in development and applications of the subsystem based formulation of density functional theory. This formulation leads to the orbital-free embedding formalism which is designed to be applied for large polyatomic systems in such cases where only a small part requires a high-accuracy quantum mechanical level of description [Wesolowski and Warshel, *J. Phys. Chem.*, *97* (1993) 8050]. Previously, we applied it to study: a) IR spectra of probe molecules in zeolites, b) the molecules physisorbed on different surfaces, c) the effect of the environment on the proton transfer process in liquids and enzymes (for review, see [Wesolowski, *CHIMIA*, *56* (2002) 707]). We use computer simulations to address some of the fundamental issues of density functional theory (approximating the kinetic energy functional and describing the energetics of weakly overlapping electron densities) as well as to apply the developed formalism in practical modelling. Typically, such studies of small model systems do not involve too significant computational efforts and can be performed using our local resources. In some studies, however, occasional access to high-performance resources proved to be of inestimable value for our research. For instance, *i*) to obtain reference benchmark results for smaller systems, *ii*) to apply our formalism for large systems, or *ii*) to obtain reference data derived from other formalisms. The projects involving the calculations performed in Manno, and their current status are listed below.

Achievements

A) We finished a comprehensive analysis of the accuracy of various approximations to the total energy bi-functional $E[\rho_A, \rho_B]$. For a large number of weakly interacting intermolecular complexes, the interaction energies derived form our formalism have been compared with high-level *ab initio* benchmark results [1]. It was shown, that the approximation to the bi-functional of the generalized gradient approximation type developed previously in our group [Wesolowski *J. Chem. Phys.*, *106* (1997) 8516] and tested on a small number of systems remains a very good approximation in a wider class of intermolecular complexes.

B) We applied the developed approximation in the studies of intermolecular complexes formed by large planar heterocyclic complexes -potential building blocks of conducting nanocolumns. These studies allowed us to determine the structural preferences in such complexes [2]. The structure corresponding to the global minimum is shown in Figure 57.

C) Although we are quite satisfied with the accuracy of the approximation to the bi-functional $E[\rho_A, \rho_B]$ developed so far, we intend to improve it further. To this end, it is very important to distinguish two types of effects affecting the obtained energies: the technical ones (the basis sets) and the real physical ones (describing the energetics of weakly or non-overlapping electron densities by means of explicit functionals of the electron density). Recently, we finished the comprehensive analysis of the effect of the basis sets on the energies derived using the total energy bi-functional $E[\rho_A, \rho_B]$ [3].

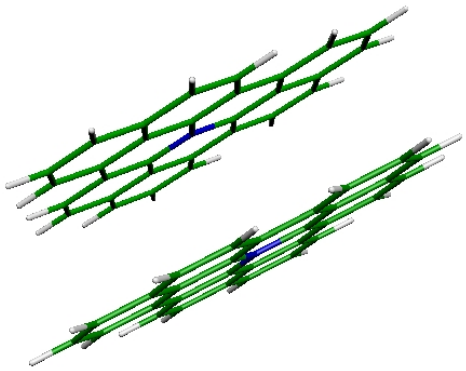

Figure 57: The minimum energy structure of the $(C_{30}H_{15}N)_2$ dimer.

D) We started a project aimed at the determination of the mechanism of binding of uranyl to various organic anions. In the first stage, we applied the conventional Kohn-Sham formalism to determine the structure of the uranyl-salophene complexes [4]. We intend to continue this project and to use our orbital-free embedding formalism in the studies of the properties of weaker complexes.
E) We analyzed the energetic balance between the $\pi - \pi$ and hydrogen-bonding in several weak complexes involving phenol. To this end, we applied our method based on the total-energy bifunctional [5].
F) One of the most CPU-time consuming sub-project, in which we apply the orbital-free embedding formalism to study IR spectra of various molecules (CO_2, CO, CO..CO) adsorbed in ZSM5 zeolite is in its final state.

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Project title: **DNS and LES of multi-fluid flows and heat transfer**

Project leader: G. Yadigaroglu, D. Lakehal

Researchers: M. Fulgosi, P. Liovic

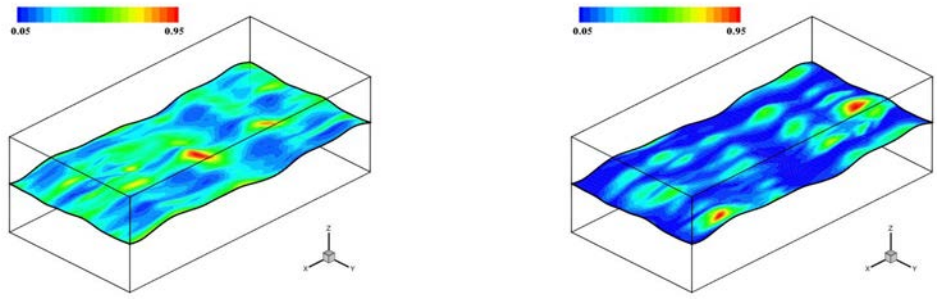
Institutions: Nuclear Engineering Laboratory, ETH Zürich

Description

The overall research aims at advancing the knowledge on the turbulence at interfaces separating immiscible fluids and associated heat transfer with or without phase change.

DNS framework

Pseudo-spectral Direct Numerical Simulation (DNS) is used for the investigation of condensation of pure steam onto subcooled water (DCC) in a stratified gas–liquid flow [1, 2, 3]. Different flow conditions have been studied, varying the degree of subcooling in the water and the deformation of the interface. The goal is to extract information on the modification on the turbulence induced by condensation, and to obtain correlation for the heat transfer coefficient. The condensation is seen to considerably reduce the turbulence in the vapor phase, which in turn implies a reduction of the turbulence intensity in the liquid. As in the case of passive heat transfer, the exchange mechanisms in the vapor and liquid phases are driven by different phenomena. In the vapor phase, figure 58(a), the interfacial heat transfer distribution correlates well with the interfacial shear stress, meaning that the renewal of the fluid elements in the vicinity of the interface is dictated by the sweep-ejection cycle. On the liquid side, figure 58(b), the patterns of the shear stress and heat transfer coefficient are not correlated, and the interfacial heat transfer distribution looks more patchy than streaky, even though the renewal of fluid in the interfacial region is still mainly due to the sweep events.



(a) Vapor side. (b) Liquid side.

Figure 58: Normalized interfacial heat transfer coefficient in the presence of condensation. The vapor phase flows in the upper domain in the x direction, and the liquid flows in the opposite direction in the lower domain.

LES framework

The IBM-SP4 platform has contributed to our success in performing Large-Eddy Simulation (LES) of interfacial air–water flow using the MFVOF-3D code. Figure 59 shows instantaneous snapshots of air venting at 10 l/s. As can be seen, the use of 3D volume tracking and physical models to track all interfaces stretching, fragmentation and coalescence results in realistic simulations, which provides more physical insight into the flow than inter-dispersed-phase 2-fluids models.

Dr. Liovic has worked closely with Dr. Jean Favre (CSCS) to improve the visualization of this highly complex multi-phase turbulent flow, in particular the coherent structures developed within the flow. Figure 60 shows these structures (opaque isosurfaces) to be are concentrated in the gas-side flow. From this work, one paper has been accepted for publication and is in press [4], another two papers have been submitted for publication recently [5, 6], and a third publication will be submitted based on already-generated results.

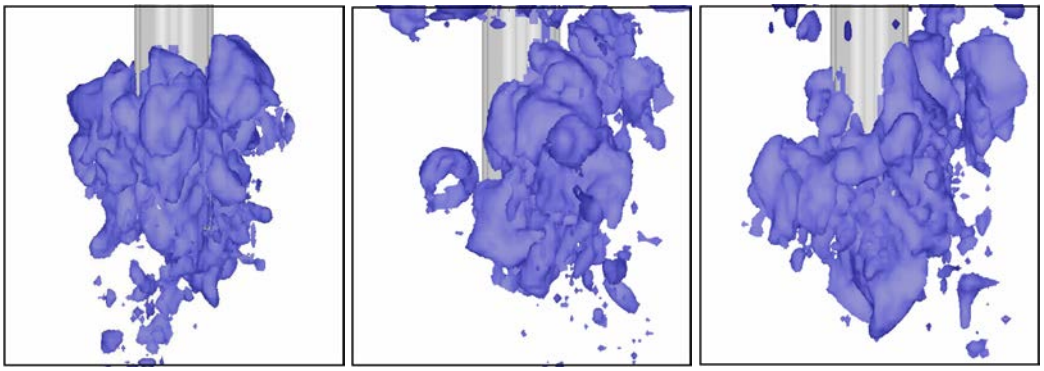


Figure 59: Frames of the bubbling resulting from air venting through a downcomer, for air flowing at 10 l/s into a water bath.

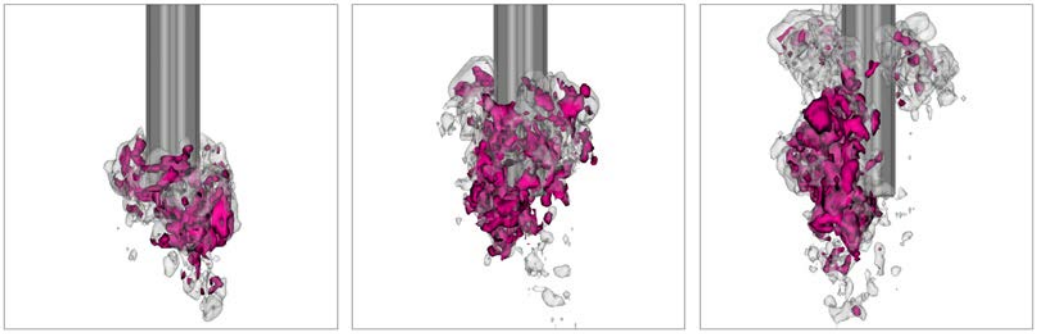


Figure 60: The isosurface of $\lambda_2 = -25000$.

In other work in this project, an advanced new 3D volume tracking (VOF) method has been developed, and a paper on this work has recently been submitted for publication [7]. Figure 61 shows piecewise planar interface reconstructions generated using our new CVTNA (Centroid-Vertex Triangle-Normal Averaging) method, for maximum deformation and upon full flow reversal on successively refined meshes. Numerical testing of the scheme demonstrates second-order accuracy even for large mesh sizes, with excellent local and global conservation properties.

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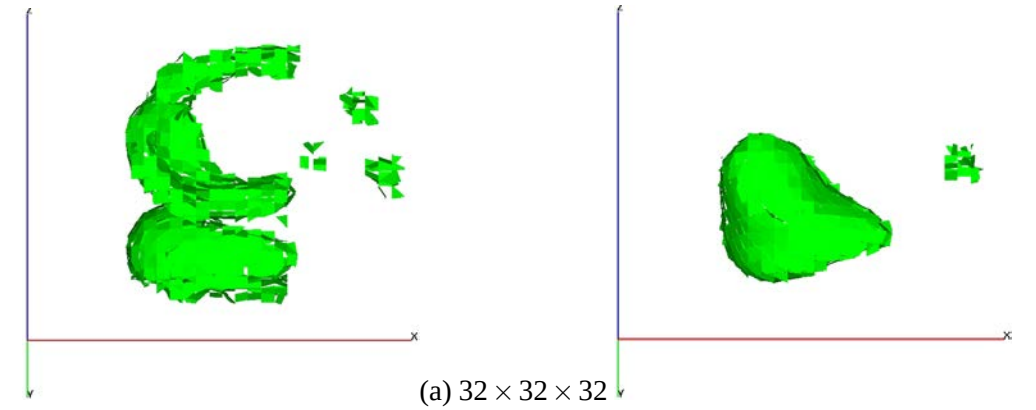
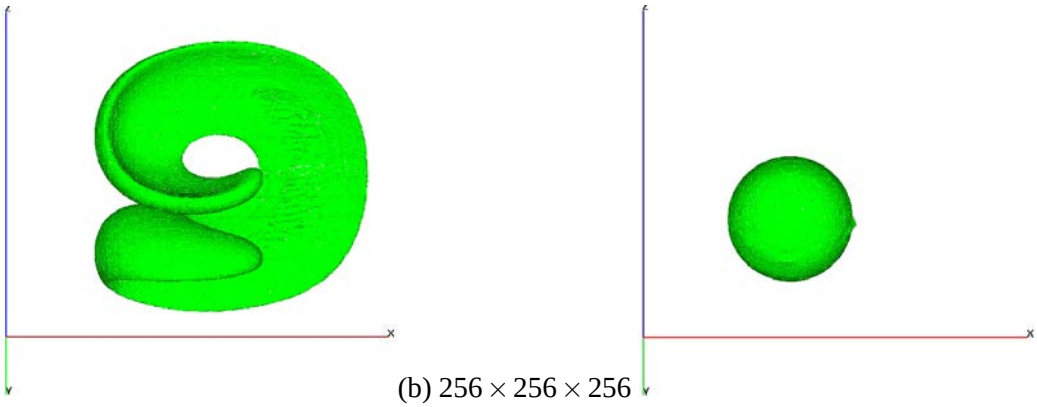


(a) $32 \times 32 \times 32$



(b) $256 \times 256 \times 256$

Figure 61: The CVTNA piecewise planar interface reconstructions on grids ranging from $32 \times 32 \times 32$ to $256 \times 256 \times 256$ grids.

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