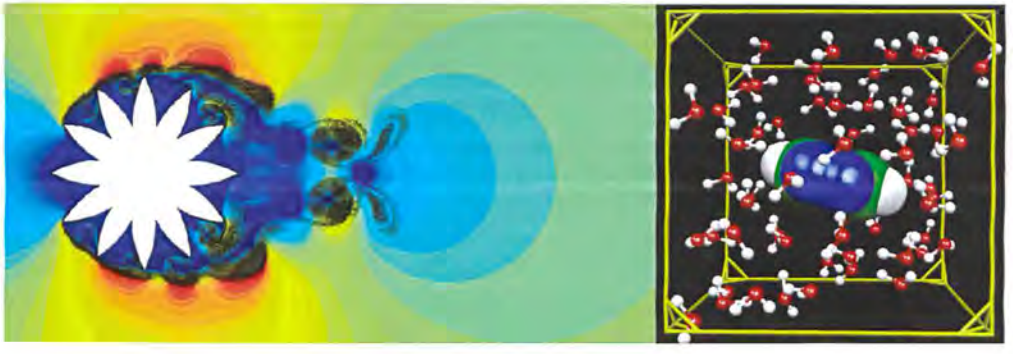
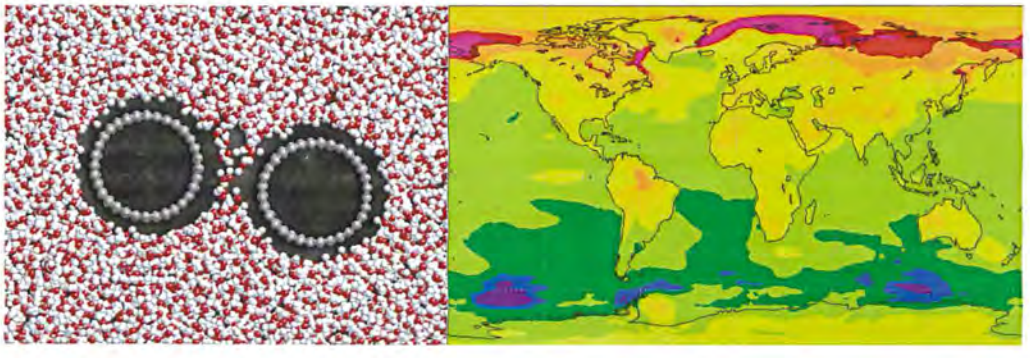
Centro Svizzero di Calcolo Scientifico

Swiss Center for Scientific Computing

# Annual Report 2001/2002





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# Contents

# Preface

In this report are collected the scientific papers made possible by CSCS computational resources. In the last two years, increased computer power has led to a much richer and more varied scientific production than before, and the Swiss computational community can look back with satisfaction on its accomplishments. I should like to take this opportunity to thank all those who have made this possible. I left the job as CSCS Director because its pressing demands were incompatible with my scientific research. The direction of CSCS has passed to the capable hands of Dr. Marie-Christine Sawley and I am sure that under her leadership CSCS will make further progress and, given the right political environment, will be able to strengthen its role in the Swiss scientific community.

Michele Parrinello

# Supercomputing Service Division

The mission of the Swiss Centre for Scientific Computing is to enable top-class computational science in Switzerland and to promote scientific computing by collaborative research and development. As science and technology centre, the CSCS provided in 2001 and 2002 leading-edge expertise in computational modeling, graphics and visualization, information processing and software engineering together with high-end computing, storage, archiving and visualization resources, services and support. The complementary expertise in enabling technologies and advanced computing resources make CSCS an attractive partner for academia, federal government agencies and industry.

**High Performance Computing and Networking Resources (HPCN)**

In 2001–2002, CSCS offered supercomputing services to the national User community on the following architectures (see Figure 1):

- 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 R11.1 with NQS scheduler. The network connection is provided via GigabitEthernet, HiPPI and FastEthernet.
- Massively Parallel Processing (MPP), with 8 IBM Regatta p-690 SMP for a total of 256 CPUs, 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 runs on AIX 5.1 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.

CSCS recognizes the importance of the close integration of supercomputing and data management and offered 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 running on a SUN E6000 file and archive server, which transparently handles data movement between the fast StorageTek 9176 raid disk cache of 2 TB and two high-capacity StorageTek Powderhorn tape silos with mixed SCSI / FiberChannel technology providing a data volume currently in excess of 150 TB.

The core architecture of the high-performance production network is based on HiPPI and GigabitEthernet technology with standard protocols (NFS, FTP, NIS). 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 has been integrated into the Swiss Academic and Research Network WAN (SWITCHlambda) ensuring the connection to CSCS's 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.

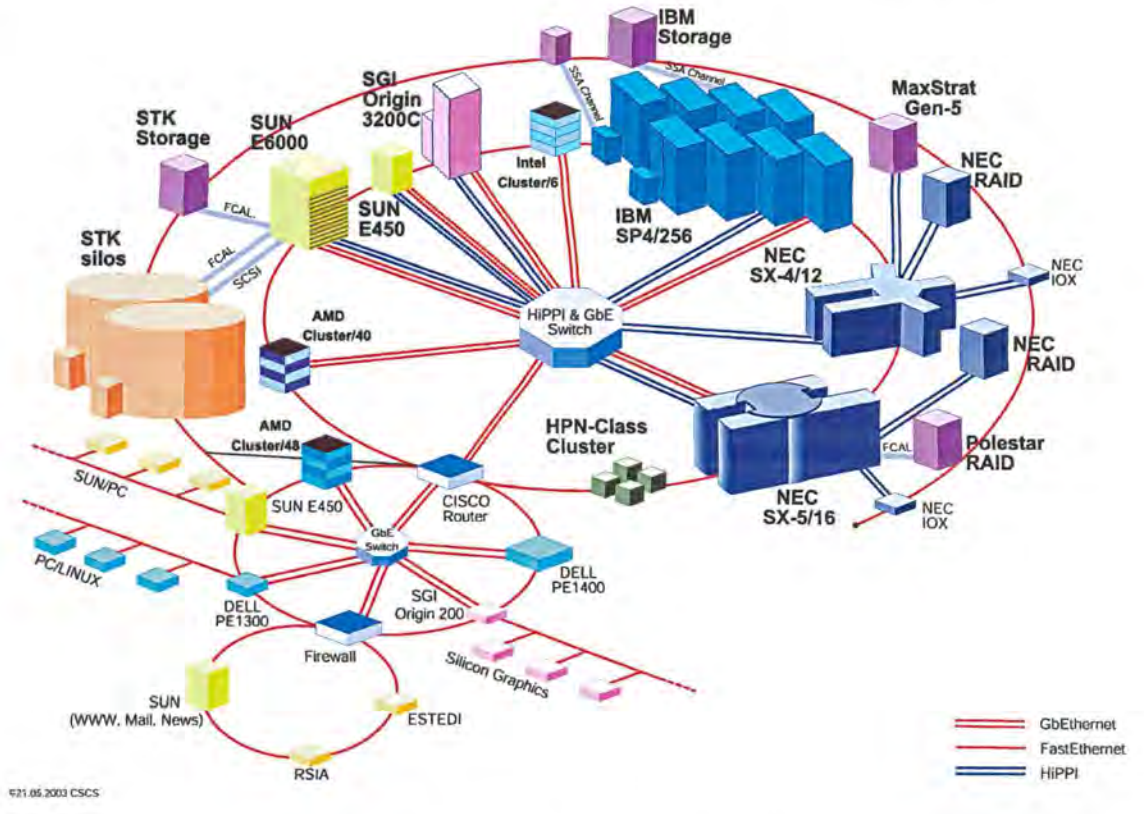


Figure 1: CSCS HPCN resources at a glance.

### User Community

The swiss community of CSCS users is widely distributed over the two Swiss Institutes of Technology and the Cantonal Universities. The group of Prof. M. Parrinello (Computational Science, ETH 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 grants access to the supercomputing resources.

Along with Swiss academia, the federal government agencies implied in national security related to environment (Figure 2) benefit significantly from CSCS's service thanks to the ongoing collaboration with MeteoSwiss and the National Competence Centre in Research (NCCR) for Climatology. 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 99% availability over the year. (http://www-users.cscs.ch). Furthermore, CSCS has also provided MeteoSwiss with the optimization and vectorization of the latest developments of the aLMo code (the Alpine Local Model), which was done by tuning the code on the parallel-vector architecture reaching a significant efficiency (30–40% on NEC SX-5).

### HPCN Service highlights in 2001/2002

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 has pursued a selected number of projects needed for the future development of the Service (selected EU and KTI projects incl.


Figure 2: The MeteoSwiss-CSCS collaboration joint coordination team.

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

*HPC Systems Support:*
The major success project of 2002 was the installation of the CSCS IBM Massively Parallel Processing (MPP) supercomputing facility, as a complement to the existing CSCS NEC SX-5 Parallel Vector Processing architecture, and the finalization of the system configuration. After the successful completion of the system acceptance phase, the new supercomputing platform was opened for full production to the whole User community from 1st January 2003.

This new MPP platform is composed of 8 IBM Power4-based Regatta nodes (SP4 system, see Figure 3), and 2 IBM Power3-based Nighthawk SMP nodes (SP3 system) dedicated to the research group of Prof. Parrinello. The SP4 nodes are switched by a fast double IBM Colony Switch to allow the highest internode communications, and the local high-performance network connections were based on GigabitEthernet and HiPPI technologies. By means of the Logical Partitioning feature, each Regatta node was partitioned in four logical nodes of 8 CPUs each.

The new MPP was installed in several steps starting from January 2002. During the system acceptance phase, which thoroughly tested the MPP system for functionality, performance and availabil-

Figure 3: IBM SP4 system.

ity, a restricted community of Pilot-Users was allowed to run production activity on the system. By constantly monitoring the system activity, a lot of information was collected with regard to usage patterns and system performance under various system configurations; the continuous interaction with the Pilot-Users provided many inputs that enabled to determine the best system resources partitioning as well as the queuing and scheduling of Users' jobs via LoadLeveler.

The major effort and achievement has been the full integration of the new MPP system into the CSCS HPCN production environment. The detailed technical documentation for Users has been significantly extended to cover the new IBM system, and made available on-line to all CSCS Users.

*HPC Application Support:*
One of the major efforts of 2002 was spent on the software installation on the IBM MPP platform, in order to provide Users with both emerging and latest versions of commercial applications; particular focus was also put on the porting and tuning of User applications as well as on the overall User programming and execution environment.

Targeting an efficient and effective use of the overall HPC facilities, the application support team consolidated and completed the Computational Chemistry Framework as well as the Mathematical and Numerical Libraries. The available portfolio now covers a wide algorithms/methods spectrum including: - Libraries and Tools; Vampir, MathKeisan, ASL, GPFA, NAG, NetCDF, FISHPACK, Zufall, ESSL, FFTW, LAPACK, MASS, P-ESSL, ScaLAPACK, WSMP, GA Toolkit, TurboMP,

hpmcount, NAGWare, MLIB, VECLIB, Mathematica, Matlab and Maple. - Chemistry Applications; ADF, CPMD, Gamess-US, Gaussian98, Amber, Dalton, GROMACS, JAGUAR, MPQC, NWCHEM, TURBOMOLE, WIEN2K, MolPro, Molcas, MELDF-X and PRDDO/M. - Engineering Applications; STAR-CD, CFX and FLUENT.

In the frame of the collaboration between CSCS and MeteoSwiss, the major achievement include the set-up of a real-time meteorological observational database, which is currently employed operationally to better define the initial conditions for the simulations, and is also being used for climatology research and analysis of past extreme events.

Finally, a considerable effort has been provided to process incoming day-by-day Users support requests as well as the consolidation and regular update of technical documentation available under the CSCS User web portal.

*HPC Benchmarking and Development:*
The major focus has been in the permanent evaluation of emerging HPC hardware technologies, with particular attention on current and future requirements of CSCS strategic users and their applications. Exploratory benchmarking activities of representative codes like LM and CPMD have been the basis for defining application performance targets for CSCS supercomputers. This permanent technology evaluation process based on key user applications provides the basis for efficient planning and anticipation of CSCS HPC resource upgrades or new acquisitions.

Particular efforts have also been made in the development of specialized system monitoring tools, with focus on sustained performance aspects. After the development of the world-wide used "qscan" utility developed at CSCS for NEC SX systems over the last years, a new "performance environment" for IBM Power4 based systems has been developed, consisting of a set of client and server daemons permanently measuring runtime system, jobs and process performance. IBM users can automatically and easily get job information and statistics including performance, during execution and after completion. In addition, the server can optionally generate very compact process accounting files, that can be easily post-processed. For example, on a heavily loaded 256 CPU system, a single accounting file of 1.5 MB size can cover more than 95% of daily system activity data. To our knowledge, CSCS is the only site to date able to globally monitor system, processes and job performance of IBM Power4 Clusters.

In conjunction with the development of the Performance Environment, a java based tool has been developed in order to easily generate resource usage reports of the CSCS HPC platforms via GUI or in batch mode. 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 order to extend 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 whilst using the acquired know-how to build a brand new product based on the LM weather forecast code able to deliver weather forecasts on demand in a grid environment.

The EUROGRID project aims to build a European Grid infrastructure that gives Users a seamless, secure access to High Performance Computing resources and that drives computational science in Europe. The CSCS has been directly involved in the "HPC Research GRID" as well as in the "Meteo-GRID" work packages of this project. The first work package consists in establishing a European GRID network of leading High Performance Computing centers from different European countries, while the second work package's goal is to exploit the power of the established grid in order to support on-demand weather forecasts. For this purpose, a LM plug-in

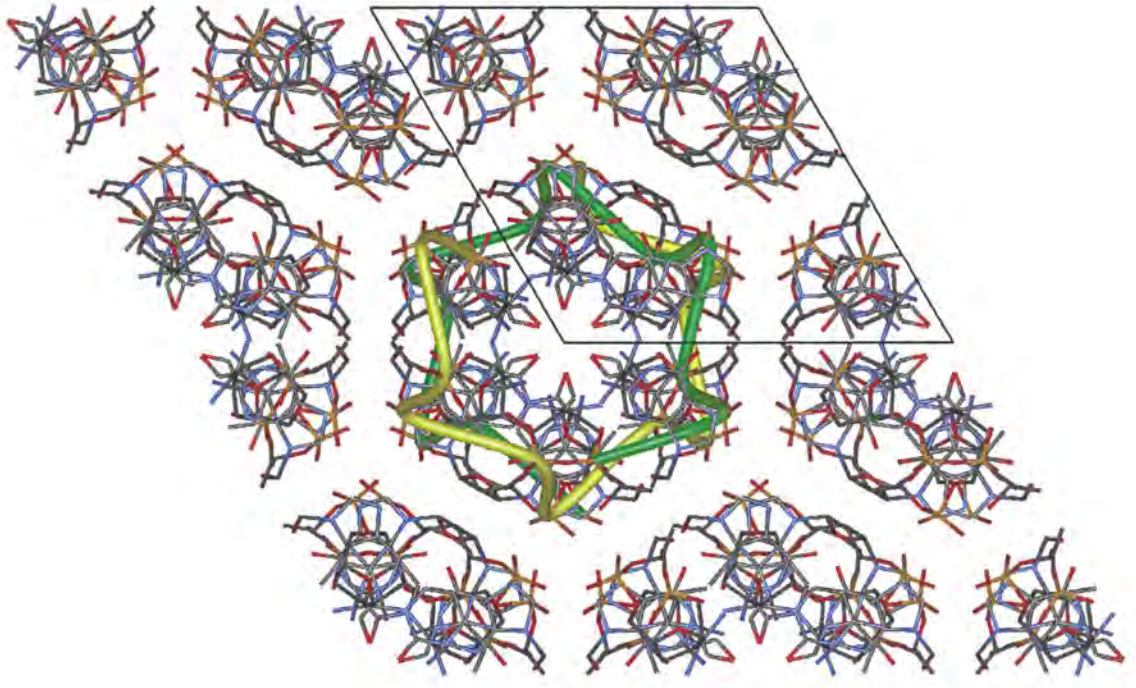

Figure 4: DNA crystal structure.

application extending the basic functionality of the EUROGRID software was developed, enabling high-resolution short-range weather forecasts with the relocatable non-hydrostatic "Lokal-Modell" (LM) of the Deutscher Wetterdienst (DWD).

The ENACTS (European Network for Advanced Computing Technology for Science) project aims at evaluating future development trends of computational science and its pan-European implications. The outcome of the first year activities, the reports "Grid Service Requirements" and "HPC Technology Roadmap" are currently available for download. The CSCS contributed to these activities with the "Grid Enabling Technology" report written together with the Foundation for Research and Technology-Hellas (FORTH) in Greece.

**Advanced Scientific Visualization:**

The Scientific Visualization activities were concentrated on two main projects: first, the development based on AVS/Express of a Molecular Visualization toolkit which allows the rapid prototyping of visualization scenarios and visualization methods for molecular sciences (Figure 4). The toolkit is used internally to support the activities of Prof. Parrinello and was distributed in source code to MPI Dresden, U. of Dortmund, INRIA, and ETH Zürich. Secondly, a completely automatic chain of visualization outputs was created for the daily runs of Swiss Meteorology. The development consisted in including a Lagrangian Eulerian Advection algorithm in AVS/Express to provide spatially and temporally correlated animation sequences of wind data (Figure 5) [1,2,3]. This work was later released to the community as an open-source contribution.

Support for CFD in general remained a priority [4]. The group continued its efforts in generic development of tools and environments with the evaluation of the AMIRA software, a study of Direct Manipulators User Interface widgets in VTK, a major effort at understanding and applying Volume Rendering techniques, and a strong effort at using SMP and MPI for parallel visualization

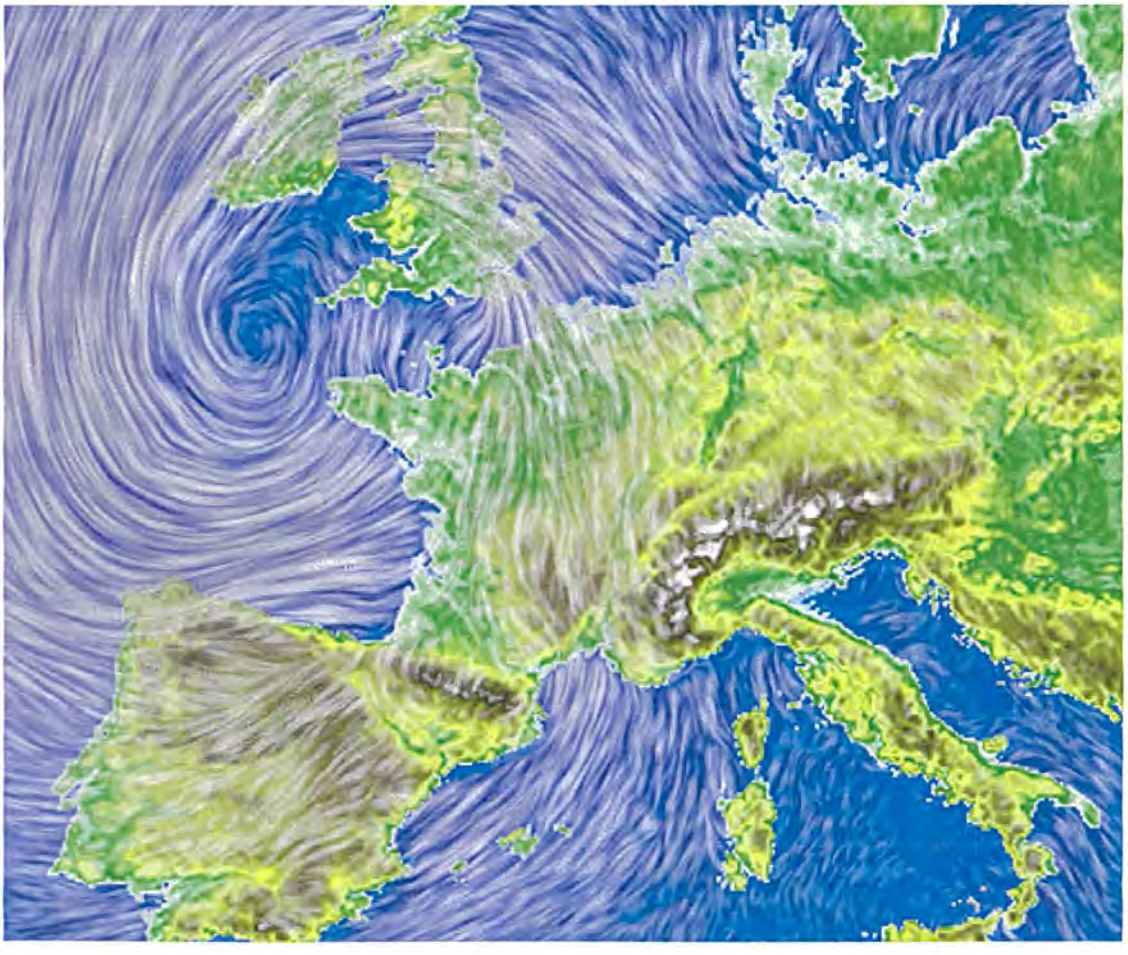

Figure 5: Wind velocity textures over Europe.

and rendering.

In 2001, the group organized and co-chaired the European EUROGRAPHICS Visualization and Simulation conference in Monte Verita [5,6]. Finally, the group also contributed to the international research community with reviews for IEEE Transactions on Computer Graphics and Visualization and IEEE Computer Graphics and Animation; as well as with committee duties for the 2002 European Visualization and Simulation conference, and the 2002 Eurographics Workshop on Parallel Graphics and Visualization.

**References**

[1] B. Jobard, G. Erlebacher, and Y. Hussaini, IEEE Transactions on Visualization and Computer Graphics **8**, 211 (2002).

[2] B. Jobard et. al, 8th Workshop on Meteorological Operational Systems, ECMWF at Reading (UK), Nov. 12–16 (2001).

[3] B. Jobard, G. Erlebacher, and Y. Hussaini, Proceedings of IEEE Visualization 2001, San Diego, California (2001).

[4] P. Leyland, J. M. Favre, S. Merazzi, A. Henze, and H. Olivier, CIMNE, Barcelona, Spain

(2002).

[5] D. Ebert, J. M. Favre, and R. Peikert, in *Computers & Graphics, Special topic "Visualization of Very Large Datasets"*, Guest Editors, **26**, 207 (2002).

[6] D. Ebert, J. M. Favre, and Ronny Peikert, Proceedings Editors of Visualization and Simulation 2001, Ascona, Switzerland (2001).

# Science Division (Research Group Parrinello)

The following is a representative selection of the research projects performed by the Science Division at CSCS lead by Prof. Michele Parrinello.

**Project title:** Oxidative damage of DNA

**Researchers:** F. Gervasio

**Description**

through computer simulation we study the oxidative damage to DNA, which is a common cause of mutagenesis, cancer and cell death. Since guanine (G) has the lowest oxidation potential among nucleic acid bases and holes can travel long distances along the DNA strands, it is believed that guanine radical cation ($G^+\cdot$) is the first step in the oxidation process [1]. The subsequent steps are much less clear. The aim of this study is to elucidate the complex chemical reactions that take place after the formation of $G^+\cdot$ and to assess whether or not there is an energetic funnel that guides the oxidation process toward a single product. Achieving this goal requires taking into account the complex environment in which the oxidation process takes place (Figure 6). To this effect we use state-of-the art molecular dynamics simulations, taking advantage of large computational resources and novel computational methods. In particular, we have used an efficient and accurate QM/MM method [2] and the novel metadynamics approach [3], which allows long time scale phenomena to be studied. We conclude that DNA is engineered in such a way that at the end of the oxidation process a single product is generated, namely 8-oxoguanine.

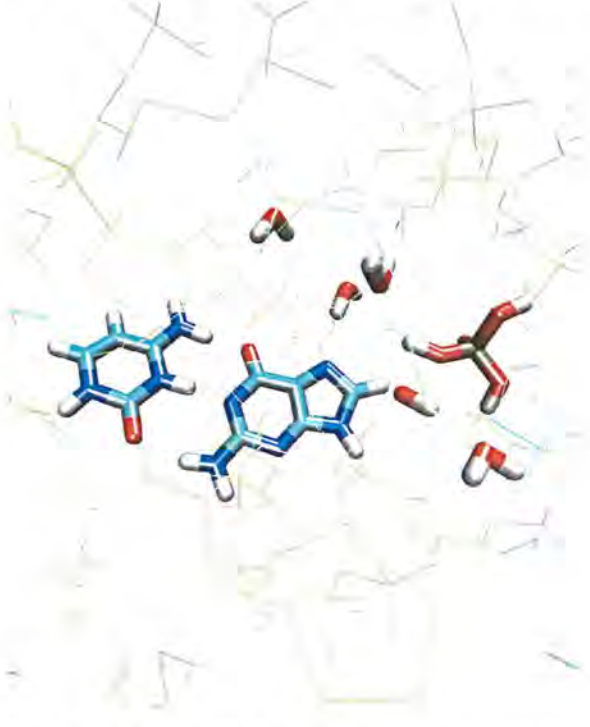

Figure 6: The time limiting step of the oxidation reaction is depicted. The quantum sub-system is highlighted.

**References**

[1] S. Steenken, Chem. Rev. **89**, 503-520 (1989).

[2] A. Laio, J. VandeVondele, and U. Röthlisberger, J. Chem. Phys. **116**, 6941-6947 (2002).

[3] A. Laio and M. Parrinello, PNAS 99, 12562 (2002).

**Project title:** Theoretical study of dehydration-carbonation reaction on brucite surface based on ab initio quantum mechanic calculations

**Researchers:** S. V. Churakov

### Description

The carbonation of brucite ($Mg(OH)_2$) has been considered as a potential technology for cleaning industrial carbon dioxide waste. The kinetics of the reaction $Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$ has been studied experimentally at 573°C by Bearat at al. [1]. Their experiments suggest that the carbonation of magnesium hydroxide proceeds by the reaction $Mg(OH)_2 \rightarrow MgO + H_2O$ followed by the absorption of $CO_2$ molecules on the dehydrated brucite surface. Due to the large difference in volumes between $Mg(OH)_2$ and MgO, dehydration causes the formation of dislocations and cracks, allowing water molecules to leave the brucite surface and facilitating the advance of the carbonation front in the bulk solid. The detailed mechanism of this process is however unknown. We used the Car-Parrinello ab initio molecular dynamics method to study the structure and dynamics of the (0001), (1-100) and (11-20) surfaces of brucite and calculated the enthalpy and activation barrier of $H_2O$ nucleation and dehydration on different surfaces. The reactive Car-Parrinello molecular dynamics method [2] has been applied to investigate the detailed mechanism of the dehydration-carbonation reaction at the (1-100) interface of brucite with the gas phase. The detailed mechanism of initial dehydration step on the (1-100) surface, followed by carbonation is shown in Figure 7. The mechanism of the carbonation, and the carbonation induced dehydration is the matter of ongoing research.

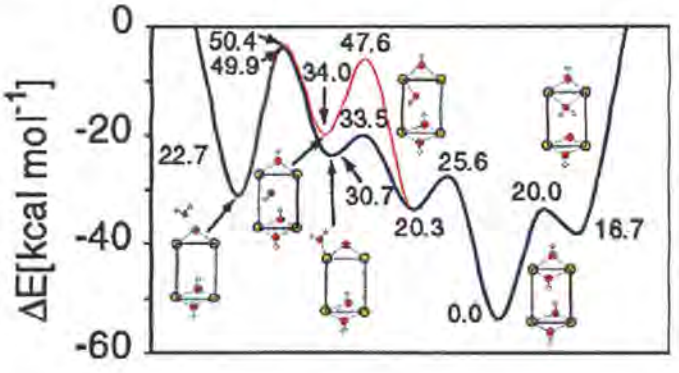


Figure 7: Free energy profile of dehydration reaction on the (1-100) surface of brucite. Geometry of the configurations corresponding to local minima of free energy at 300 K are shows schematically (Mg-yellow; red; H-white). Number near the minima and transition states indicate the free energy in kcal $mol^{-1}$ measured relative to the ground state energy of the (1-100) surface.

### References

[1] H. Bearat, M. J. McKelvy, A. V. G. Chizmeshya, R. Sharma R, R. W. Carpenter, J. Amer. Ceram. Soc. **85**, 742 (2002).

[2] M. Iannuzzi, A. Laio, and M. Parrinello, Phys. Rev. Lett. **90**, 238302 (2003).

**Project title:** Fast density functional calculations with QUICKSTEP

**Researchers:** M. Krack
F. Mohamed

### Description

This project focuses on the development and the efficient implementation of new quantum-chemical methods based on density functional theory (DFT). In the recent years DFT has become a very efficient tool for electronic structure calculations, since DFT methods are fast and their accuracy is comparable to sophisticated ab-initio methods for many properties. One such method is the Gaussian plane waves (GPW) method [1] that uses two types of basis functions: (1) Gaussian-type functions for the description of the Kohn-Sham orbitals and (2) plane waves as an auxiliary basis set to expand the electronic charge density in order to combine the merits of both types of basis functions.

A new, efficiently parallelized implementation of the GPW method, called QUICKSTEP, is developed in the framework of this project. QUICKSTEP is a sub-project of the open source project CP2K (http://developer.berlios.de). CP2K is a program package written in Fortran 95 including both classical and quantum-chemical codes. Efficiency and parallelism of the codes were considered from the very beginning and all codes share the same basic data structures. QUICKSTEP shows a quasi-linear scaling for the calculation of the Kohn-Sham matrix. Therefore larger system sizes or longer simulation runs are feasible. Figure 8 shows the crystal structure of a fully hydrated RNA duplex which is a standard test system for QUICKSTEP (368 atoms, 3456 basis functions). The IBM SP4 system serves as an excellent development and benchmarking platform for the parallelized implementation. Recently, the QUICKSTEP code was also successfully applied for the calculation of the x-ray scattering spectra of liquid water at different temperatures [2].

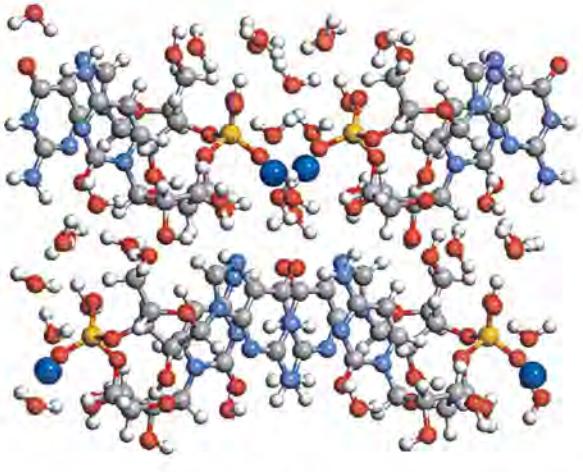

Figure 8: Unit cell of the crystal structure of a fully hydrated RNA duplex ($C_{76}H_{168}N_{32}O_{84}Na_4P_4$).

### References

[1] G. Lippert, J. Hutter, and M. Parrinello, Mol. Phys. **92**, 477 (1997).

[2] G. Hura, D. Russo, R. M. Glaeser, T. Head-Gordon, M. Krack, and M. Parrinello, Phys. Chem. Chem. Phys. **5**, 1981 (2003).

# Large User Projects

**Project title:** First-principles computations of growth-related defects and molecular nanostructures

**Project leader:** A. Baratoff[1]

**Researchers:** A. Catellani[2]
L. Pizzagalli[3]
G. Cicero[4]
A. Alkauskas[1]

**Institutions:** [1]Institut für Physik, Universität Basel
[2]CNR-IMEM, Parma
[3]Laboratoire de Métallurgie Physique, Université de Poitiers
[4]INFM-Dipartimento di Fisica, Torino

**Description**

In 2002 most of the computations performed on the NEC SX5 at CSCS focused on elucidating the atomic structure and the resulting electronic properties of the (001) epitaxial interface between cubic SiC and Si [1]. The 20% lattice mismatch SiC is accommodated via an array of mutually perpendicular edge dislocations. Density functional calculations performed on the NEC SX5 on a system of almost 300 atoms with periodic boundary conditions yield trustworthy results. Plausible dislocation core structures were first investigated using classical molecular dynamics on the same system, as well as on much larger ones; the most favorable structures were then used as inputs to the CPU-intensive ab-initio computations. The classical simulations relied on an empirical potential validated by comparison with previous ab-initio studies, e.g. [2]. The most stable interface structure depicted in Figure 9 has 13 instead of 25 carbon atoms at the interface. It exhibits no dangling bonds, but electronic trap states localized near the dislocation cores which may degrade

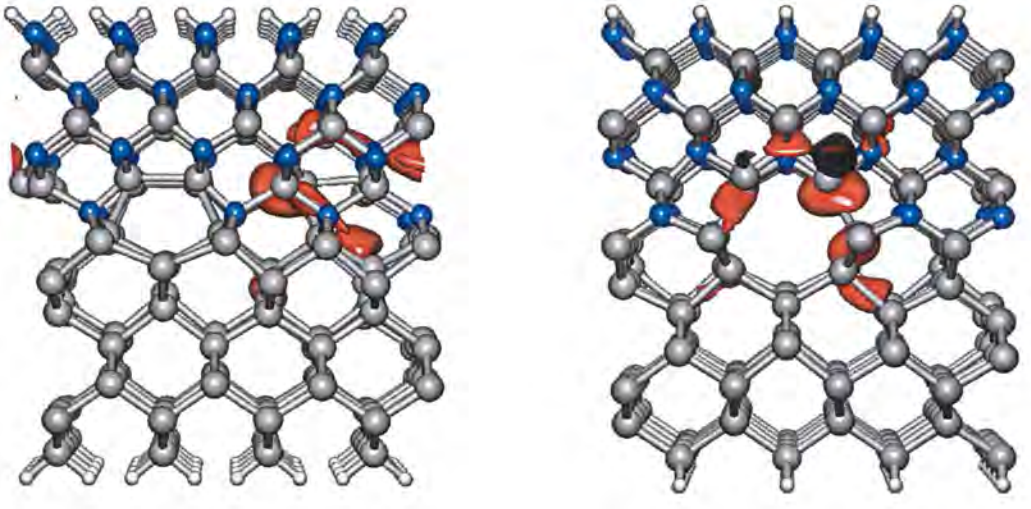

Figure 9: Si/SiC interface structure.

the performance of thin film SiC devices grown on Si(001). On the other hand preliminary computations indicate that a pseudomorphic SiC bilayer on SiC(001) transforms upon relaxation into a puckered disordered layer with Si-C bond lengths close to those of bulk SiC.
A PhD student hired in May within the Molecular Machinery project of the NCCR on Nanoscale Science is becoming familiar with the CPMD code of M. Parrinello and coworkers. He will use it to understand the adsorption and self-organization of Subpthalocyanine and similar polar molecules studied by STM at U. Basel [3].

**References**

[1] G. Cicero, L. Pizzagalli, and A. Catellani, Phys. Rev. Lett. **89**, 156101 (2002).

[2] A. Catellani and G. Galli, Progress in Surface Science **69**, 101 (2002).

[3] M. deWild et al. ChemPhysChem, in print.

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

**Project leader:** M. Beniston[1]

**Researchers:** S. Goyette[1]
E. Koffi[1]
B. Koffi[1]
J. P. Blanchet[2]
M. Verstraete[3]

**Institutions:** [1]Climate Modeling Group, Department of Geosciences, University of Fribourg
[2]University of Quebec, Montreal
[3]JRC-ISPRA, Italy

**Description**

The CESIA project (3.1) 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, four 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. Franziska Keller (doctoral student, funded by the University of Fribourg - i.e., own contribution - and working on alpine vegetation response to climatic change), Ms. Paula Casals (funded by the Swiss Agency for the Environment, Forests and Landscape, BUWAL - i.e., third-party funding, 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). A succinct summary of the status of the research projects are given below.

- *Regional Climate Modeling (RCM) of extreme wind-storms*
  Considerable effort has been made since the previous NCCR report to finalize earlier studies; in particular, a crucial element in the simulation of wind-storms is the parameterization of gusts. Gustiness generally results in more damage on trees and infrastructure than mean wind velocities, so that in order more adequately simulate areas where damage may be important in economic terms, the problem of wind gusts needs to be addressed within the framework of an RCM. Two approaches can be envisaged: an empirical, observation-based approach, and a physically-based approach that enables the estimation of wind gusts from a newly-developed parametric scheme.

  The nowcasting and prediction of strong winds are still far from adequate, whether they are based on statistical or on numerical modeling approaches. During the last decade, Switzerland has been exposed to two major extra-tropical storms, namely the February 1990 storm "Vivian", and the December 1999 storm "Lothar", that caused severe damage to infrastructure and to forests. Although numerical weather prediction models captured the cyclone tracks on the synoptic scale in both case, the severity of local gusts was not properly reproduced over Switzerland. To help predict such phenomena, a combined approach to diagnose the wind gust speeds over Switzerland was described in a paper recently published by Jungo, Goyette and Beniston (2002) in Int. J. Clim. The diagnostics aim at computing the probability of exceedence of a particular gust threshold based on the mean wind in relation to the prevailing synoptic weather types for a number of Swiss climatological stations. Based on ten years of observations, the computation of this probability uses an empirical gust factor, which is a function of the daily gust speed, itself a function of the daily mean wind speed. Each day has been categorized into

three weather types according to the Schüpp classification. Principal Component Analysis and Cluster Analysis are performed in order to group climatological stations having similar characteristics in daily wind gust velocities. The results show that the gust factor provides an accurate method to compute the daily wind gust speeds at each Swiss climatological station for the given period. The proposed diagnostics thus represent an efficient empirical method to predict the distribution of wind gust speeds.

In terms of physically-based approaches to the problem, an innovative "off-line" method was proposed by Brasseur (2001) to compute wind gusts. The approach has been implemented as an "on-line" subgrid-scale parameterization in the Canadian CRCM-2 model used in the context of NCCR-Climate at the University of Fribourg (Goyette, Brasseur and Beniston, 2002, submitted to J. Geophys. Res.). The method assumes that gusts occurring at the surface result from the deflection of air parcels moving at higher elevations within the boundary layer. The trigger mechanism for this deflection is attributed to turbulent eddies. Since no "ideal" theoretical cases with known analytical gust solutions exist, the parameterization has been tested with real data from well-documented wind-storms. In order to illustrate the performance of this novel method, the 1990 "Vivian" and the 1999 "Lothar" storms have been simulated with the Canadian RCM at various resolutions. Preliminary analysis indicate that this parameterization performs well over both flat and mountainous terrain; the scheme responds properly in the strengthening as well as the weakening phases of wind storms. However, the storm-dependent results are also a function of the model configuration during the self-nesting procedure. The spatial and temporal distributions of the simulated gusts are thus seen to depend on the accuracy of the simulated flow fields.

- *Response of alpine vegetation to changing snow cover*
  The PhD-project of Ms. F. Keller focuses on the relation between the duration of mountain snow pack and the response of high alpine vegetation at the start of the vegetation period. The melting of the snow cover determines the onset and length of the growing period of the vegetation. The study is structured into two parts:
  1. a botanical part, by Prof. Christian Körner (Botanical Institute, University of Basel);
  2. a climatological part supervised by Prof. M. Beniston and Dr. S. Goyette (Department of Geosciences, University of Fribourg).

  In the botanical part of the project, laboratory experiments were carried out with 33 high-alpine species to test their sensitivity of growth and flowering with respect to day length and temperature. For the thermal sensitivity, groups of species preferring warm or cold temperatures were differentiated. Regarding the "length-of-day" experiments, groups of species insensitive to day length, species requiring long days (i.e., late spring/summer) and those that respond to short days (i.e., late winter/early spring) were distinguished. A paper that discusses these results has recently been submitted by Keller and Körner to Arctic, Antarctic and Alpine Research.

  In 2002, the main focus has been on the numerical investigations of the snow cover change. Investigations of the current behavior of the snow pack at various altitudes, as a complement to the modeling study, have been summarized in 2002 by Beniston, Keller and Goyette in a paper that is currently in press in Theor. and Appl. Clim. In parallel, a snow parameterization of the Surface Energy Balance Model (SEBM) developed at the Department of Geosciences of the University of Fribourg has been revised and upgraded. Secondly, a study was performed to test the sensitivity of the snow cover to an increase of mean, minimum or maximum temperatures. Simulations were carried out for two alpine stations in the eastern part of Switzerland (Säntis at 2450 m asl and Disentis at 1190 m asl). The results of this study have been submitted by Keller and Goyette as a book chapter in a volume published by J. Wiley, entitled "Hydrological and

Meteorological coupling in mountain areas: Experiments and Modeling" edited by C. de Jong, D. Collins and R. Ranzi. As intuitively expected, the mean, minimum and maximum temperature increase scenarios shorten the duration of the snow cover. This reduction occurs mostly during the snowmelt period in spring and summer. Snow accumulation in autumn appears to be a much less sensitive period of the year. In addition, the fact that precipitation falls more often as rain than as snow accelerates the melting process. The two sites exhibit significant changes in the duration of the snow pack with even in the presence of a temperature increase that is modest compared to the temperature changes predicted by the IPCC (IPCC 2001).

- *Assessment of forest damage to extreme climatic events*
  The BUWAL-funded project (Swiss Agency for the Environment, Forests and Landscape, Bern) addresses the issues of forest damage and associated hazards such as mud-slides or land-slides following the exposure of slopes that were previously protected by forest cover.

  The PhD project started in March 2002, and to date has essentially involved a bibliographic survey of extreme climatic events for the past 500 years, forest ecology and management issues, and approaches to slope stability and erosion issues. The inclusion of data in a GIS system has begun, with data available from the Swiss Federal Office of Statistics already available for geological characteristics, forest cover, and topography at a spatial resolution of 100 m.

  The project is divided into three parts. In the first part, Geographical Information Systems (GIS) techniques are used to assess zones that are at highest risk in terms of forest damage resulting from extreme events, and the possible subsequent risks for slopes, for example landslides, rock-falls, or floods. In a second part, changes in slope stability will at a later stage be undertaken using an erosion model (possibly the WEPP Water Erosion Prediction Project model) in regions where forests are vulnerable to damage by extreme events. In the third part of the project, toward the end of the funding period, results from the Canadian Regional Climate Model (CRCM-2) will be used to assess regions in Switzerland that are likely to be vulnerable to extreme climate events may be most important.

- *Other research related to extreme events*
  In the time he allocates to the NCCR-Climate, M. Beniston has conducted research of relevance to changes in extremes as related to the behavior of the North Atlantic Oscillation, and research on shifts in snow-pack characteristics as a contribution to the sub-project on mountain vegetation response to climatic change (already mentioned above, i.e., Beniston, Keller and Goyette, 2002, Theor. and Appl. Clim.).

  An investigation by Beniston and Jungo (2002: Theor. And Appl. Clim.) has been undertaken in order to assess the manner in which the North Atlantic Oscillation (NAO) influences not only general, average, climatic conditions, but also the extremes of dynamic and thermodynamic variables. By choosing representative sites in the Swiss Alps, the present study shows that there is a high sensitivity of the extremes of the probability density functions of temperature, moisture and pressure to periods when the NAO index is either highly-positive or strongly negative. When the NAO index is strongly positive, temperatures and pressure shift toward positive anomalies, and there is a general reduction in atmospheric moisture at high elevations. Furthermore, a change in typical alpine winter weather patterns can be detected during strongly positive NAO anomaly phases. The winters of the last decade of the 20th Century (1989-99) are characterized by a substantial decrease in cold advective high pressure situations and simultaneously an important increase in warm convective high pressure systems. These patterns differ significantly from the weather types, which have been recorded for earlier periods of the 20th Century. As a result of the highly-positive nature of the NAO index in the latter part of the 20th Century, it is speculated here that a significant part of the observed warming in the Alps results

from the shifts in temperature extremes induced by the behavior of the NAO. These changes are capable of having profound impacts on snow, hydrology, and mountain vegetation.

**References**

[1] M. Beniston, F. Keller, and S. Goyette, Theor. and Appl. Clim., in press (2002).

[2] M. Beniston, Dendrochronologia **20**, 117 (2002).

[3] M. Beniston, Climatic Change, accepted (2002).

[4] M. Beniston and P. Jungo, Theor. and Appl. Clim. **71**, 29 (2002).

[5] P. Jungo, S. Goyette, and M. Beniston, Int. Journal of Clim. **22**, 485 (2002).

[6] S. Goyette, M. Beniston, P. Jungo, D. Caya, and R. Laprise, Climate Dynamics **18**, 145 (2001).

[7] P. Jungo and M. Beniston, Theor. and Appl. Clim. **69**, 1 (2001).

[8] OcCC Report on the Impacts of Climatic Change for Switzerland. Contribution by M. Beniston

[9] M. Beniston, in *Advances in Global Change Research*, edited by M. Beniston (Kluwer Academic Publishers, Dordrecht, 2002), p. 503.

[10] M. Beniston and M. M. Verstraete, in *Advances in Global Change Research* new series, edited by M. Beniston (Kluwer Academic Publishers, Dordrecht, 2001), p. 356.

**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 Zurich

## Description

In a combined experimental and theoretical approach we seek to understand heterogeneous enantioselective hydrogenation by modified platinum metal catalysts, which is a promising route for the synthesis of optically pure compounds. 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 molecules [1]. We also use vibrational circular dichroism (VCD) for the structure determination of dissolved chiral modifiers and complexes between modifiers and reactant molecules [2]. As an example Figure 10 shows the experimental VCD spectra of the modifier (R)-2-(1-pyrrolidinyl)-1-(1-naphthyl)-ethanol (PNE) together with the calculated VCD spectra of the three most stable conformers. The calculations were performed at the B3PW91 level of theory using a 6-31G* basis set. Comparison between theoretical and experimental spectra shows that Open(3)' is most abundant, in agreement with the calculated relative stability of the conformers.

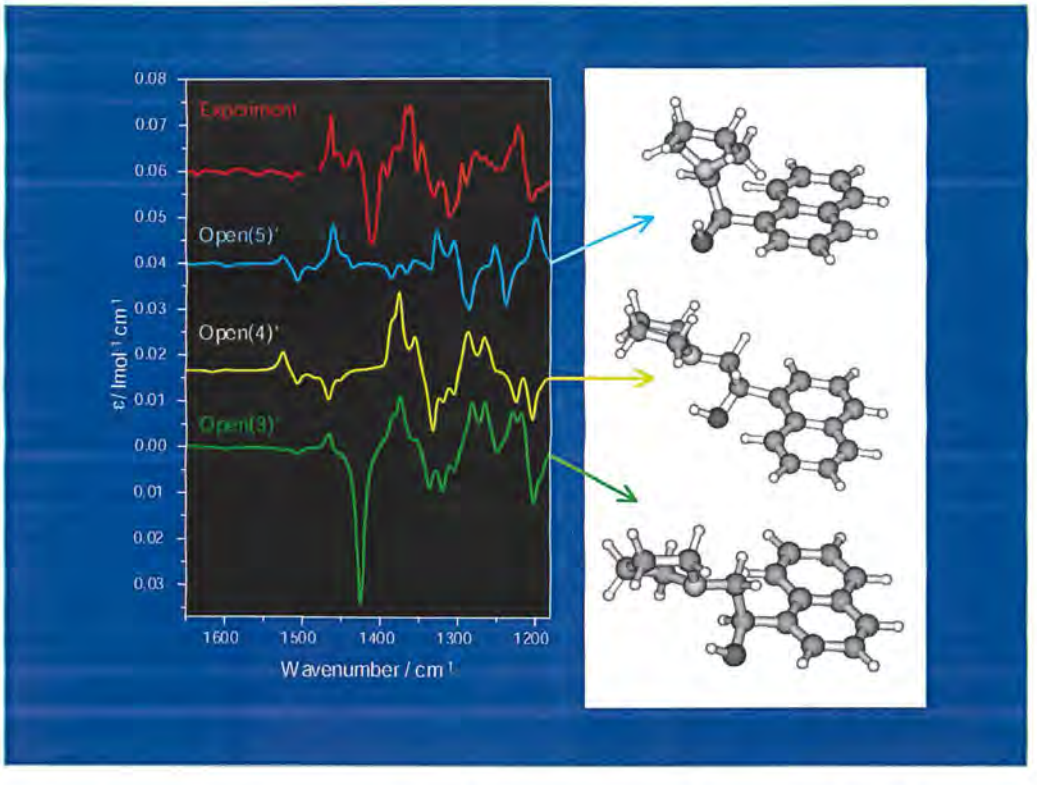


Figure 10: Experimental VCD spectra of the modifier (R)-2-(1-pyrrolidinyl)-1-(1-naphthyl)-ethanol (PNE) together with the calculated VCD spectra of the three most stable conformers.

We furthermore elaborate reactivity-electronic structure relationships for series of different substrates, in order to gain insight into the role of substitutes and modifier-reactant intermolecular interactions on reactivity [3,4,5].

**References**

[1] D. Ferri and T. Bürgi, J. Am. Chem. Soc. **123**, 12074 (2001).

[2] T. Bürgi, A. Vargas, and A. Baiker, J. Chem. Soc. Perkin Trans. **2**, 1596 (2002).

[3] A. Vargas, T. Bürgi, and A. Baiker, New J. Chem. **26**, 807 (2002).

[4] A. Vargas, T. Bürgi, M. von Arx, R. Hess, and A. Baiker, J. Catal. **209**, 489 (2002).

[5] W. R. Huck, T. Bürgi, T. Mallat, and A. Baiker, J. Catal. **205**, 213 (2002).

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

**Project leader:** P. Hasenfratz

**Researchers:** F. Niedermayer
K. Juge

**Institutions:** Institute of Theoretical Physics, University of Bern

### Description

Quantum-Chromodynamics (QCD) is one of the four known fundamental interactions. QCD is formulated in terms of quarks and gluons and is responsible for the behavior of hadrons like the proton and neutron. It has an important almost exact symmetry, the so-called chiral symmetry. This symmetry plays a major role in all low-energy hadronic processes. For traditional formulations of lattice QCD this symmetry is seriously broken which prevents simulations with light quark masses. Recent theoretical developments allowed us to construct and test a new implementation which overcomes these difficulties. Large scale numerical simulations on the Hitachi SR8000 in Munich (in the framework of the Bern-Graz-Regensburg Collaboration) and on the IBM MPP at

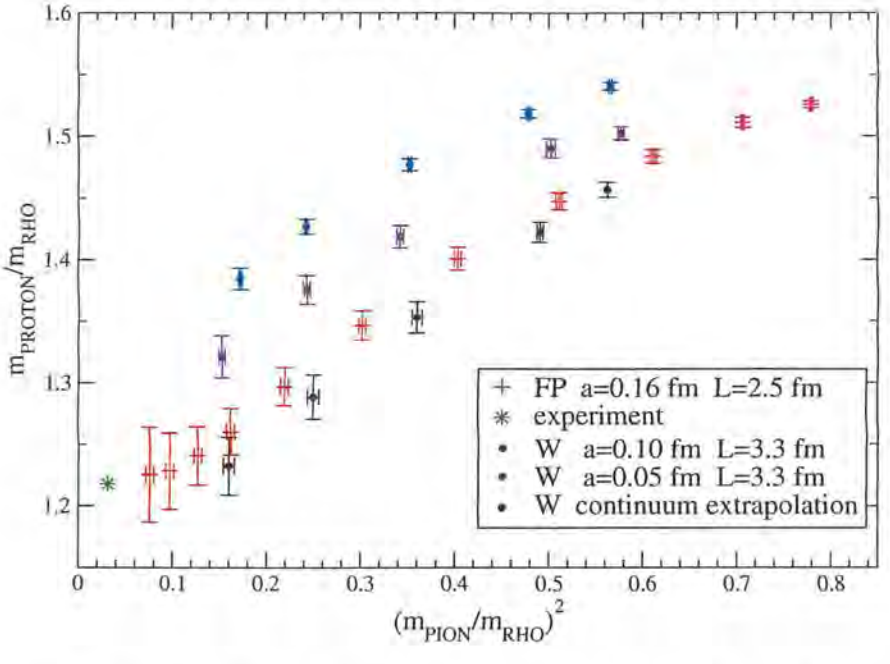


Figure 11: In QCD the value of the quark mass is a free parameter. The ratio of the nucleon mass to the rho meson mass (vertical axis) and the ratio of the pion mass to the rho mass (the square of it is on the horizontal axis) is changing as the quark mass is varied. The green star gives experimental prediction, the crosses are our results (FP), while the other sets of points (W) are the best earlier results using a traditional formulation of lattice QCD (CP-PACS, Tsukuba, Japan). As this figure shows, in our new formulation we are able to work with significantly smaller quark (and pion) masses. In addition, while the earlier results (W) show significant cut-off effects (i.e. the results strongly depend on the lattice resolution $a$), our results are close to the continuum extrapolation already on coarse lattices.

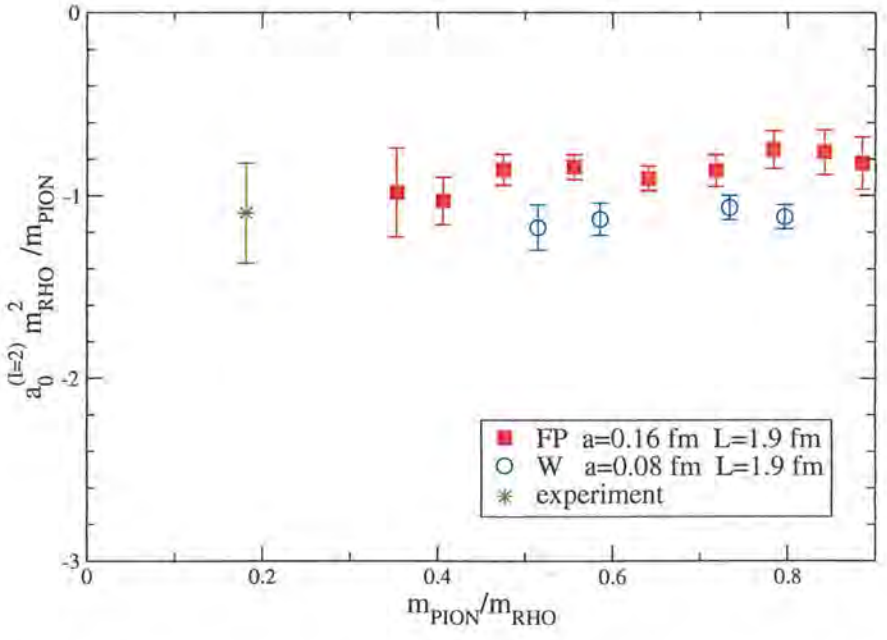


Figure 12: Close to the chiral limit — where the quark mass and, consequently, the pion mass are sufficiently small — low energy physics is determined by the properties of the lightest mesons, the pions. The pion-pion scattering at low energies (e.g. cross section, scattering phase) is characterized by the "scattering length" which is proportional to the pion mass for small pion masses. We measured the scattering length $a_0^{(I=2)}$ at different quark masses, i.e. different pion mass over rho mass ratios. The superscript $I = 2$ refers to a given channel, e.g. the $\pi^+\pi^+ \to \pi^+\pi^+$ scattering. We plotted our result (FP) for the dimensionless combination $a_0^{(I=2)} m_{\mathrm{RHO}}^2 / m_{\mathrm{PION}}$ which stays finite in the chiral limit. For comparison we also show the results obtained by the traditional lattice action (W) (JLQCD collaboration, Tsukuba, Japan) and the experimental value (green star). This figure illustrates again the good chiral properties of our action: we can get to smaller $m_{\mathrm{PION}}/m_{\mathrm{RHO}}$ ratios even at coarser lattices. The possible cut-off effects (discretization errors) have still to be investigated.

CSCS allowed us to explore different aspects of hadron physics close to the chiral limit: light hadron spectroscopy including a study of finite volume and cut-off effects, and preliminary results on the pion decay constant and scattering length.

**References**

[1] P. Hasenfratz, S. Hauswirth, K. Holland, T. Jorg, and F. Niedermayer, Nucl. Phys. B, submitted.

[2] C. Gattringer, M. Gockeler, P. Hasenfratz, S. Hauswirth, K. Holland, T. Jorg, C. B. Lang, F. Niedermayer, P. E. L. Rakow, S. Schaefer, and A. Schafer, to be published in the Proceedings of the Lattice 2002 Conference, Boston.

**Project title:** Ab initio molecular dynamics in electronically excited states

**Project leader:** J. Hutter

**Researchers:** M. Odelius

**Institutions:** Institute of Physical Chemistry, University of Zurich

### Description

We have combined density functional based methods (restricted open-shell DFT and time-dependent DFT) for the description of excited states of molecules and condensed systems with molecular dynamics [1–3]. These methods have been applied to calculate the solvent shift in the electronic spectrum of s-tetrazine in aqueous solution [4] (see Figure 13). The solvent shifts in the lowest singlet excitations of s-tetrazine in aqueous solutions are studied using ab initio molecular dynamics simulations and time-dependent density functional theory. It is seen that the large solvent shift in the S2 excitation is indeed due to polarization of the highest occupied molecular orbital, as previousl literature suggests. However, in contrast to the diazenes this orbital polarization is not due to a strong hydrogen bonding to the nitrogen atoms, instead the shift occurs simply as a consequence of the electrostatic field from the surrounding solvent molecules. It is also observed that the hydrogen bonding between water and the methenyl group in s-tetrazine is as strong as the hydrogen bonding between water and the nitrogen atoms, and both are much weaker than the internal hydrogen bonding in water resulting in a clathrate-like solvent shell structure.

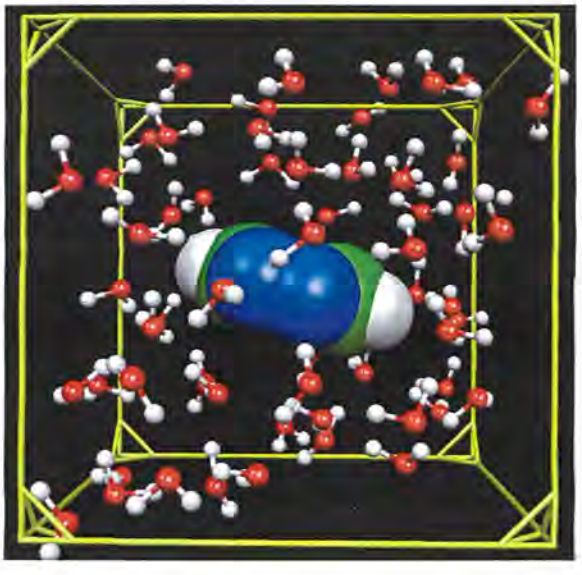

Figure 13: s-tetrazine in aqueous solution.

### References

[1] I. Frank et al., J. Chem. Phys. **108**, 4060 (1998).

[2] M. Odelius, D. Laikov, and J. Hutter, J. Mol. Structure, submitted.

[3] J. Hutter, J. Chem. Phys., submitted.

[4] M. Odelius and J. Hutter, manuscript in preparation.

**Project title:** Transition metal catalyzed reactions and Car-Parrinello molecular dynamics

**Project leader:** J. Hutter

**Researchers:** D. Gleich

**Institutions:** Institute of Physical Chemistry, University of Zurich

### Description

The aim of our project is a theoretically founded understanding of transition metal catalyzed reactions. In contrast to previous investigations, the reaction conditions (temperature, solvent, etc.) are explicitly considered. Three programs are predominantly used: Gaussian98 and ADF for static and CPMD for dynamic quantum-mechanical calculations. The common theoretical level belongs to density functional theory. We focus on rhodium-catalyzed hydroformylation (formal addition of CO and $H_2$ to a C-C double bond) which is one of the largest scale processes of industrial homogeneous catalysis and therefore especially attractive for theoretical investigations. Static DFT calculations in the gas phase with rhodium-phosphine model systems of different electronic and steric properties are linked to those of Car-Parrinello MD simulations. We also take a QM/MM coupling scheme for CPMD simulations with the sulphonated phosphine ligand tppts in water (see Figure 14). Rhodium/tppts catalysts are used in the Ruhrchemie-Rhône-Poulenc process of hydroformylation which is *the* prototype of aqueous biphasic catalysis.

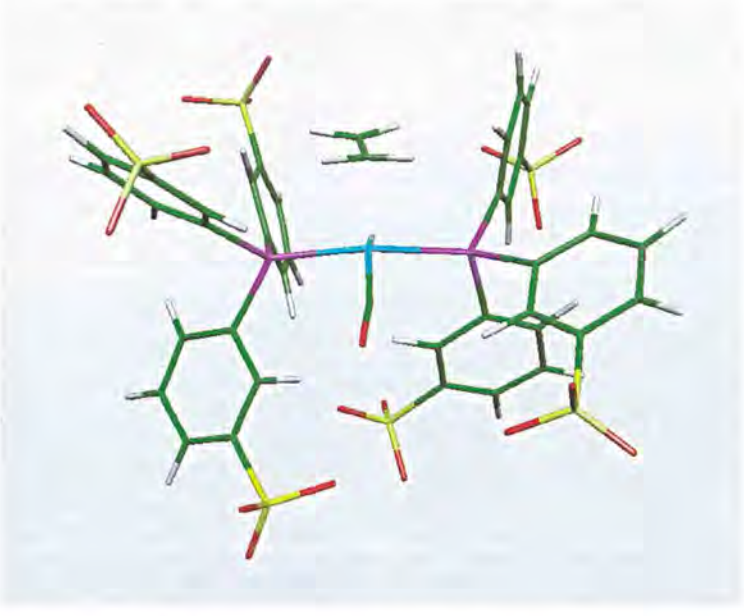

Figure 14: Sulphonated phosphine ligand tppts in water.

### References

[1] D. Gleich, in *Applied Homogeneous Catalysis with Organometallic Compounds*, edited by B. Cornils and W. A. Herrmann (Wiley-VCH, Weinheim, 2002), Vol. 2, p. 727.

[2] D. Gleich and J. Hutter, manuscript in preparation.

**Project title:** Ab initio MD study of methionine aminopeptidases

**Project leader:** C. Klein

**Researchers:** –

**Institutions:** Pharmaceutical Chemistry (Prof. G. Folkers),
Department of Applied Biosciences, ETH Zurich

**Description**

We are studying the active site of an enzyme that has considerable potential to become a pharmaceutical target protein: the methionine aminopeptidase (MetAP, see Figure 15). It is planned to use a variety of molecular modeling techniques for the design of new, selective inhibitors. A couple of questions, for example concerning the protonation state of the active site, have to be answered before serious design attempts can be undertaken. Because of the poor performance of the MM part of the QM/MM CPMD code on the NEC SX5, no simulations could be performed before the installation of the new IBM SP4 machine. After the IBM SP4 system became available, we were able to compare the dynamics and the stability of three protomers: one with two water bindings to two zinc ions in the active site, one with a bridging hydroxide between the two zinc atoms, and one with two hydroxide ions. The results clearly indicated that the di-hydroxide protomer is unstable, whereas the other two protomers can maintain stable geometries. The di-water system showed a geometric arrangement that is distinct from the crystal structure of the enzyme. When we studied this structure in more detail, it became evident that it may be more prone (as compared to the other protomer) to form a covalent adduct with fumagillin, an irreversible inhibitor of the enzyme. Subsequent experimental studies validated the presence of two distinct protonation states of the enzyme and showed that the di-water system is in fact responsible for inhibitor binding. These results will help us in designing new, irreversible inhibitors of MetAP by virtual high-throughput screening and other theoretical drug development methods.

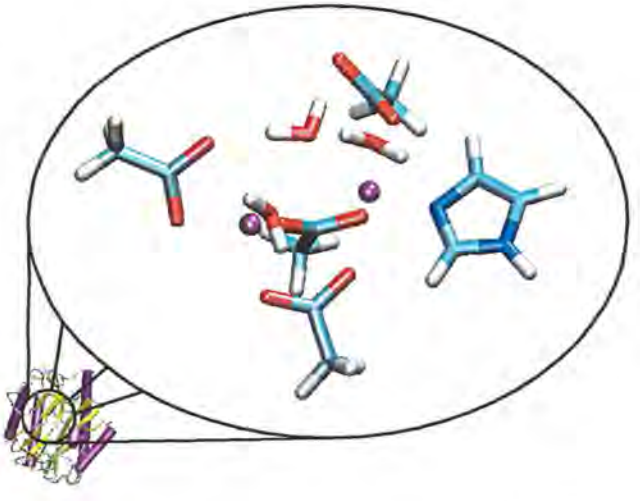

Figure 15: The core active site of methionine aminopeptidase. Only the QM atoms are shown. The small picture at the bottom shows the tertiary structure of the enzyme.

**References**

[1] P. Carloni, U. Rothlisberger, and M. Parrinello, Acc. Chem. Res. **35**, 455 (2002).

[2] C. Klein and G. Folkers, Oncology Research and AntiCancer Drug Design, in print (2003).

[3] C. Klein et al., J. Biol. Chem., submitted (2003).

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

**Project leader:** L. Kleiser[1]

**Researchers:** N. Adams[2]
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A. Jocksch[1]
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A. Kubik[1]
S. Müller[1]
M. Loginov[2]
B. Rembold[1]
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**Institutions:** [1]Institute of Fluid Dynamics, ETH Zurich
[2]TU Dresden

**Description**

In our recently developed Approximate Deconvolution Model (ADM) for LES a new approach to subgrid modeling is followed which does not make use of the conventional eddy-viscosity assumption that is known to be invalid in general. In the ADM approach, the unclosed correlations are computed directly from the approximately unfiltered flow field and the interaction between resolved and non-resolved scales is taken into account by a relaxation term. LES using ADM have 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.

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.

- *Background*
  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.

- *Sub-projects*
  1. Large-Eddy Simulation of wall-bounded flows and shock-turbulence interaction
     - In order to handle complex geometries, an existing code was extended to allow multiblock computations.
     - A high Reynolds-number supersonic turbulent boundary layer was computed in order to provide input data for the high Reynolds number compression ramp computation which is under preparation.
     - The approximate deconvolution model (ADM) was implemented in the semi-industrial Navier-Stokes multi-block flow solver NSMB. Compressible channel flow was computed successfully with ADM using a low-order finite volume scheme as a first test case. Excellent agreement of the LES results with the Direct Numerical Simulation (DNS) data was obtained. Following this initial test, an investigation of a more demanding flow configuration was started with shock-turbulence interaction on a compression ramp.
  2. Large-eddy simulation of jet flows
     In this sub-project two physically different flow situations are studied:
     - Rectangular jet flow
       In the past period different in flow conditions for the jet flow were considered, in order to study the in flow effect on the down-stream development of the jet. Particularly, turbulent in flow conditions have been applied, for which turbulent data were generated using a separate compressible duct-flow simulation, results of which were then fed into the jet simulation code. In a prior study the duct-flow code was validated with data from literature. We find a significantly faster up-breaking of the jet with turbulent in flow data compared to laminar in flow with only weakly growing linear instabilities.
       The investigation of acoustic radiation from jets has also been started within this subproject. We computed the far-field sound from LES simulations of the rectangular jet flow and made comparison with the radiation obtained from DNS data for the same case. The radiation computed from the DNS data was as expected for the chosen jet parameters and the LES was well able to reproduce the low frequencies of the radiation. However, unphysical spurious noise was found in the LES at higher frequencies that spoils the correct prediction of the radiation pattern.
       A video animation of the simulated rectangular jet flow was produced in cooperation with Dr. Favre of CSCS.
     - Large-Eddy Simulation of flows in cylindrical geometries
       The main activities in the report period consisted of additional theoretical investigations of forced and decaying isotropic incompressible turbulence aimed at a better understanding of the behavior of ADM as a modeling strategy.
  3. Simulation of turbulent particulate flows
     - Particle-laden isotropic turbulent flows:
       The implemented pseudo-spectral method with Lagrangian particle tracking was optimized for parallel computations on the SX-5 and validated for one-way coupled isotropic flows. A two-way coupling algorithm for the simulation of the particle influence on the ambient carrier fluid was implemented and validated. As a first test case for laminar two-way coupled flows at low Reynolds numbers (as opposed to high Reynolds number, turbulent flows), the settling of a cloud of particles (suspension drop) under gravity was investigated. The results were compared with data available in the literature. Fur-

thermore, the limitations of the employed particle model were examined in detail using simple flow configurations with single particles.

- Particle-laden flow over a backward-facing step:
  A Lagrangian particle description was implemented in an existing spectral-element code and validation computations on simplified cases of particle-laden flows were conducted. In a first study spatial distribution of particles in low Reynolds number flows over a backward-facing step was investigated. In addition effects of different wall-particle interaction models on the computational results were examined.

4. Large-Eddy Simulation of boundary layers with pressure gradient and separation
   - Different standard transition scenarios in incompressible channel flow have been considered with both LES and DNS computations and extensive comparison has been performed. Different alternative formulations of ADM, which was used as subgrid-scale model, have been proposed and studied. Furthermore, a new method to allow for Fourier discretization of spatially growing flows has been described and compared against the more widely established fringe-domain technique. A detailed report on this method has been written and a journal publication is under preparation. Finally, a shared-memory parallel version of the fully-spectral channel flow code has been developed.

**References**

[1] N. A. Adams, Int. J. Num. Meth. Fluids, **39**, 783 (2002).

[2] N. A. Adams and S. Stolz, J. Comput. Phys. **178**, 391 (2002).

[3] F. Graf, E. Meiburg, and C. Härtel, J. Fluid Mech. **451**, 261 (2002).

[4] A. Kubik and L. Kleiser, Proc. Appl. Math. Mech. **2**, to appear (2003).

[5] F. Necker, C. Härtel, L. Kleiser, and E. Meiburg, Int. J. Multiphase Flow **28**, 279 (2002).

[6] F. Necker, C. Härtel, L. Kleiser, and E. Meiburg, submitted (2002).

[7] B. Rembold, N. A. Adams, and L. Kleiser, International Journal of Heat and Fluid Flow **23**, 547 (2002).

[8] B. Rembold, N. A. Adams, and L. Kleiser, Proc. Appl. Math. Mech. **1**, 280 (2002).

[9] B. Rembold and L. Kleiser, Proc. Appl. Math. Mech. **2**, to appear (2003).

[10] H. J. Schmid, S. Stolz, and H. Buggisch, Flow, Turbulence and Combustion **68**, 689 (2002).

[11] S. Stolz and N. A. Adams, submitted (2002).

[12] S. Stolz, N. A. Adams, and L. Kleiser, Proc. Appl. Math. Mech. **1**, 282 (2002).

[13] S. Stolz and K. Horiuti, submitted (2002).

[14] R. von Känel, N. A. Adams, L. Kleiser, and J. B. Vos, submitted (2002).

[15] R. von Känel, N. A. Adams, L. Kleiser, and J. B. Vos, Journal of Fluids Engineering, to appear (Dec. 2002).

[16] D. Wilhelm, C. Härtel, and L. Kleiser, to appear in J. Fluid Mech. (2002).

[17] D. Wilhelm and L. Kleiser, J. Sci. Computing **17**, 619 (2002).

[18] L. Brandt, P. Schlatter, and D. S. Henningson, in *Advances in Turbulence IX*, edited by I. P. Castro, P. E. Hancock, and T. G. Thomas (CIMNE, 2002), pp. 17–20.

[19] F. Necker, C. Härtel, L. Kleiser, and E. Meiburg, in *Proc. Symposium on Sedimentation & Sediment-Transport* (Monte Verità, 2002).

[20] S. Müller, N. A. Adams, S. Stolz, and L. Kleiser, in *Advances in Turbulence IX*, edited by I. P. Castro, P. E. Hancock, and T. G. Thomas, (CIMNE, 2002), pp. 591–594.

[21] B. Rembold, J. Freund, and M. Wang, in *Proceedings of the Summer Program 2002*, (Stanford University, 2002), Center for Turbulence Research, to appear.

[22] B. Rembold and L. Kleiser, in *Proceedings LES for Acoustics*, edited by T. Hüttl, C. Wagner, and J. Delfs (DGLR-Report, 2002-03)

[23] S. Stolz, N. A. Adams, and L. Kleiser, in *Advances in LES of Complex Flows*, edited by R. Friedrich and W. Rodi (Kluwer, 2002), pp. 33–47.

[24] R. von Känel, N. A. Adams, L. Kleiser, and J. B. Vos, in *Proceedings of the 40th AIAA Aerospace Sciences Meeting and Exhibit* (Reno, NV, 2002), paper AIAA 2002-0284.

**Project title:** Multi-scale simulations using particle methods: Toward the development of multiscale computations for biosensors

**Project leader:** P. Koumoutsakos

**Researchers:** S. Attinger
J. Walther
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I. Sbalzarini
T. Werder
U. Zimmerli
R. Jaffe
G. H. Cottet

**Institutions:** Institute of Computational Science, ETH Zurich

**Description**

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 scales in problems under consideration. Particle methods are robust and enjoy automatic grid adaptivity, but carry a high computational cost which nominally scales with the square of the number of computational elements ($N$) — an N-body problem. We have implemented multipole algorithms using tree data structures and hybrid particle-mesh algorithms [1] to reduce the computational cost to $\mathcal{O}(N)$ and $\mathcal{O}(N \log N)$ depending on the complexity of the algorithm.

The studies involve MD simulations of the carbon nanotubes in an aqueous environment [2,3,4]. Figure 16A shows the hydrophobic interaction of two carbon nanotubes in water. The interaction potentials used in these MD simulations are calibrated by considering the experimental macroscopic contact angle of a water droplet on graphite cf. Figure 16B [5]. We are furthermore performing density functional theory calculations in collaboration with Prof. Parrinello of CSCS of the water-graphite system to derive the interaction potentials ab initio cf. Figure 16C [6,7,8].

Macro-scale studies include diffusion in the Endoplasmic Reticulum using three-dimensional particle methods [9] (Figure 16D), smooth particle hydrodynamics method for the simulation of fluid-structure interaction in soft tissue (Figure 16E), particle (vortex) methods simulations of particulate flows (Figure 16F) [9], and two-dimensional vortex methods using immersed interface methods [10] for the study the flow past cacti (Figure 16G).

**References**

[1] J. H. Walther, J. Comput. Phys., accepted (2002).

[2] T. Werder, J. H. Walther, R. Jaffe, T. Halicioglu, F. Noca, and P. Koumoutsakos, Nano Letters **1**, 697 (2001).

[3] J. H. Walther, R. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Phys. Chem. B **105**, 9980 (2001).

[4] J. H. Walther, R. Jaffe, T. Werder, T. Halicioglu, and P. Koumoutsakos, in *Proceedings of the summer program 2002*, Center for Turbulence Research, Stanford Univ. and NASA Ames, in preparation (2002).

[5] T. Werder, J. H. Walther, R. L. Jaffe, T. Halicioglu, and P. Koumoutsakos, J. Phys. Chem. B, accepted (2003).

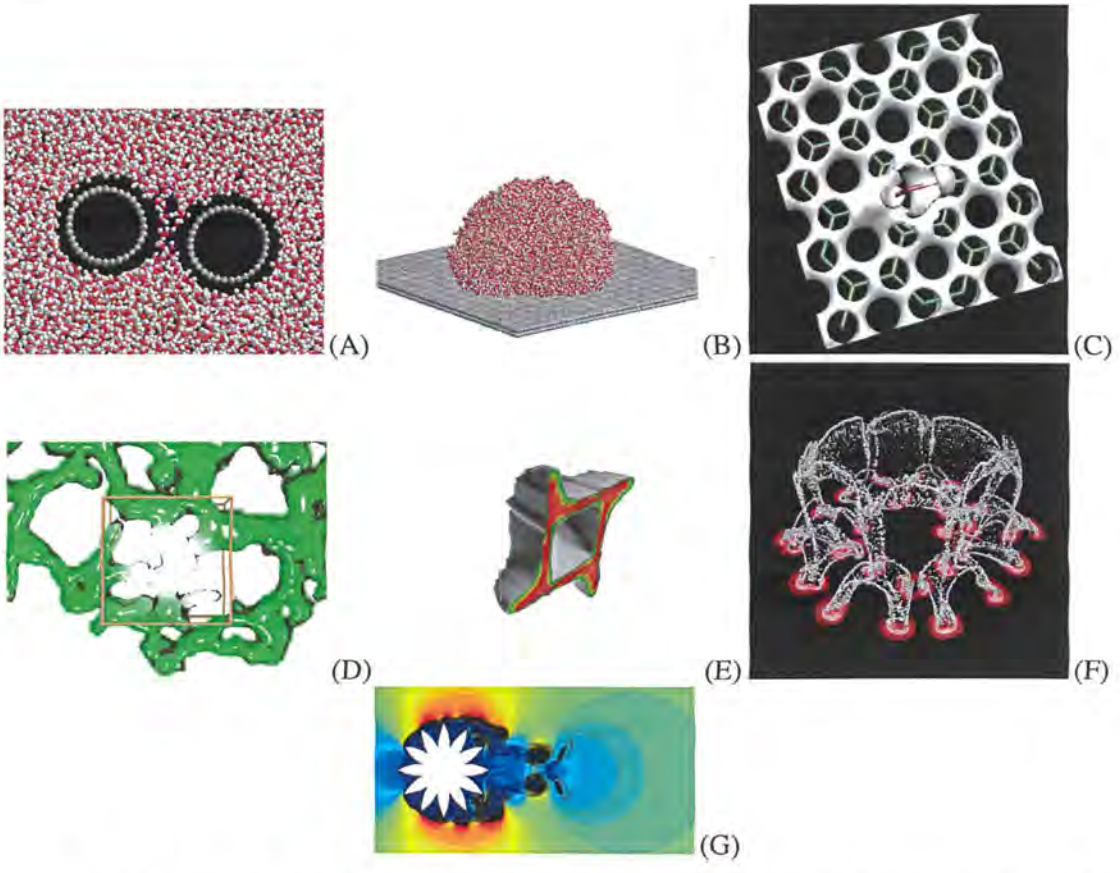


Figure 16: The pictures show (A) a snapshot from molecular dynamics simulations of the hydrophobic hydration of carbon nanotubes in water. The interaction potentials governing the molecular dynamics simulations are calibrated from studies of the macro-scale contact angle of nanoscale water droplets on graphite (B) and through density functional theory calculations (C). A parallel particle method is used for studies of diffusion in biological, geometrically complex surfaces such as the Endoplasmic Reticulum (D). Smooth particle hydrodynamics is employed for fluid-structure interactions. The picture (E) shows a test problem involving a dynamically deforming shape in a varying velocity field. A novel P3M algorithm is used for 3D simulations of charged particulates (F), and in the context of immersed interface methods for 2D bluff body flows (G).

[6] U. Zimmerli and P. Koumoutsakos, in *Fifth World Congress on Computational Mechanics*, July 7–12, Vienna, Austria (2002).

[7] P. Koumoutsakos, R. Jaffe, T. Werder, J. H. Walther, and U. Zimmerli, in *Nano Tech 2003*, p. ? (2003).

[8] U. Zimmerli, Internal report, Institute of Computational Science, ETH Zurich (2003).

[9] I. F. Sbalzarini and P. Koumoutsakos, Biophys. J., submitted (2002).

[10] J. H. Walther and P. Koumoutsakos, J. Comput. Phys. **167**, 39 (2001).

[11] J. H. Walther and G. Morgenthal, J. Turbulence **3**, 1 (2002).

**Project title:** Machine learning algorithms and applications

**Project leader:** P. Koumoutsakos

**Researchers:** N. Schraudolph
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**Institutions:** Institute of Computational Science, ETH Zurich

**Description**

We are developing data based modeling and optimization algorithms in the broad area of machine learning. Specific topics of research include biologically inspired optimisation, multiobjective design optimization of turbo-machines, machine learning algorithms for flow modeling and control, and rapid stochastic gradient descent methods for large nonlinear systems.

- *Biologically Inspired Optimisation*
  We are developing robust, massively parallel, biologically inspired optimisation strategies that are well suited for addressing complex, non-linear engineering problems. Our algorithms are based on principles such as those of biological evolution and bacterial chemo-taxis [5], and include procedures for adapting the parameters of the strategies themselves (meta-learning). We approached meta-learning from two perspectives: (i) We deployed known rules for adaptation from the algorithm and let the rule be learned during optimisation using concepts from machine learning [3,4], and (ii) we devised a novel evolutionary algorithm (the modified CMA algorithm) that collects, using large populations on highly parallel computer architectures, curvature information about the function being optimized in reduced time complexity (see Figure 17). These methods are being applied on technically relevant optimisation problems such as film cooling, jet mixing, nanofluidics, turbine blade design, and the design of micromixing devices [2].
- *Multiobjective 3D Design Optimization of Turbo-machinery*
  We are exploring the automated optimisation of various components of large-scale stationary gas turbines with respect to multiple design objectives. Gas turbine combustors are improved by coupling optimisation algorithms such as Evolution Strategies in an automated fashion with an experimental test rig. We determine the set of Pareto solutions for the trade-off between emissions and thermo-acoustic pulsation, to be reduced for environmental and lifetime reasons, respectively. For gas turbine compressor blades we are improving aerodynamic performance as well as mechanical and manufacturing aspects. We collaborate with Alstom Power Technologies, Ltd. to develop the appropriate automated optimisation tools. We focus on creating efficient tools for industrial applications comprising evolutionary algorithms and response surface techniques where measurements are noisy and/or expensive, for designs involving lengthy CFD simulations and/or prototype test runs [9].
- *Machine Learning Algorithms for Flow Modeling and Control*
  Machine learning algorithms such as neural networks and evolution strategies are computationally attractive for modeling and control of flows as they are inherently parallel and can take advantage of concurrent computer architectures. We are developing and implementing machine learning algorithms on problems of turbulent flow modeling and control. Present studies involve (i) the application of nonlinear neural networks trained by novel stochastic gradient methods to

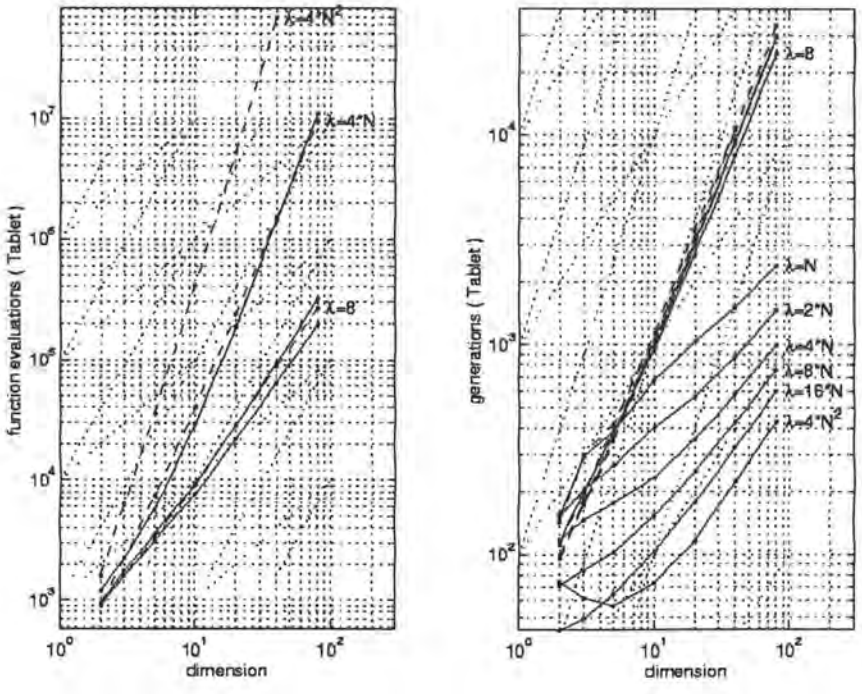


Figure 17: Number of function evaluations (left) and number of generations (right) against the problem dimension for the tablet function, for the original (– – –) and modified CMA algorithms (—).

develop near wall models for turbulent flows, and (ii) development of optimisation algorithms for drag reduction in bluff body flows, using self-organizing neural networks and novel types of genetic algorithms [6,7].

- *Rapid Stochastic Gradient Descent Methods*
  Current machine learning problems often require the stochastic optimization of large, nonlinear, differentiable, adaptive systems. However, to date there are no efficient and reliable algorithms to do this. We are developing methods such as our recent stochastic meta-descent (SMD) algorithm that fill this gap. They iteratively construct stochastic approximations of second-order gradient steps from fast curvature matrix-vector products obtained by automatic differentiation. Our current efforts focus on how to make these rapid, scalable methods stable and reliable without sacrificing their superior performance [8].

## References

[1] S. D. Müller, N. Hansen, P. Koumoutsakos, *Proceedings of the Seventh International Conference on Parallel Problem Solving from Nature (PPSN VII)*, Lecture Notes in Computer Science (Springer, Berlin, 2002), Vol. 2439, pp. 422-431

[2] S. D. Müller, P. Koumoutsakos, *Manipulation and Control of Transverse Jets*, International Centre for Mechanical Sciences (CISM), Udine, Italy, 2002

[3] S. D. Müller, N. N. Schraudolph, P. Koumoutsakos, N. Hansen, in *Workshop Proceedings of the Genetic and Evolutionary Computation Conference (GECCO-2002)* (Morgan Kaufmann Publishers, San Francisco, CA, 2002), pp. 161-164

[4] S. D. Müller, N. N. Schraudolph, P. Koumoutsakos, in *Proceedings of the Congress on Evolutionary Computation (CEC 2002)*, pp. 151-156 (2002)

[5] S. Müller, J. Marchetto, S. Airaghi, P. Koumoutsakos, *IEEE Transactions on Evolutionary Computation*, Vol. 6, No. 1 (2002)

[6] M. Milano, P. Koumoutsakos, J. Computational Physics **175**, 79-107 (2002)

[7] M. Milano, P. Koumoutsakos, J. Computational Physics (2002)

[8] N. Schraudolph, Neural Computation **14**, 1723-38 (2002)

[9] D. Büche, P. Stoll, R. Dornberger, P. Koumoutsakos, IEEE Trans. Systems, Man and Cybernetics (2002)

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

**Project leader:** S. Leutwyler[1]

**Researchers:** A. Müller[1]
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D. Henseler[1]
M. Losada[1]
C. Manca[1]
H. M. Frey[1]
M. Meuwly[2]

**Institutions:** [1]Department of Chemistry and Biochemistry, University of Bern
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**Description**

Our Large User Project is divided into four sub-topics, several of which are aimed at complementing laser spectroscopic experiments on finite-size hydrogen-bonded clusters in supersonic beams with state-of-the art quantum chemical calculations. These calculations support and complement the analysis of the spectroscopic data. Other sub-topics provide deeper understanding of hydrogen bonding, proton transfer energetics and proton transfer 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. We have shown experimentally that in supersonic jet-cooled 7-HQ·$(NH_3)_n$ clusters with $n \geq 5$, proton transfer (PT) occurs toward and along a network of ammonia molecules, whereby the cluster acts as 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. Extended *ab-initio* density functional calculations of the PT reaction paths of the $n = 6$ cluster allowed to distinguish Grotthus-type PT steps, which occur at the ends of the ammonia wire, from large-scale diffusive reaction steps which involve hydrogen bond reorganization in the center of the ammonia wire [1,2]. Analogous calculations on the $n = 4,5$ clusters are in progress.
- *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·$(NH_3)_n$, $n = 1-4$ clusters, using correlated electronic structure methods, both density functional (PW91, B3LYP) and MP2. The goals are to determine the cluster structure based on the experimental rotational constants [3,5], to calculate accurate binding energies [4], and to assign the experimental vibronic spectra [3]. Thus, the 1-naphthol·$(NH_3)_2$ cluster has an O-H$\cdots$NH$_3\cdots$NH$_3$ hydrogen-bonded chain with two conventional H bonds and an unconventional third N-H$\cdots\pi$ H bond to the $\pi$-electron cloud of the aromatic ring [5].
- *Subproject C: Hydrogen bonding in nucleobase pair analogues*
  Complementary to our spectroscopic studies on nucleobase pair analogues such as (2-pyridone)$_2$, 2-hydroxypyridine·2-pyridone, and (2-amino-6-pyridone)$_2$, 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. With the hybrid B3LYP density functional and the 6-311++G(2d,2p) basis set we have so far observed excellent agreement between the calculated and measured intermolecular frequencies of nucleobase dimer

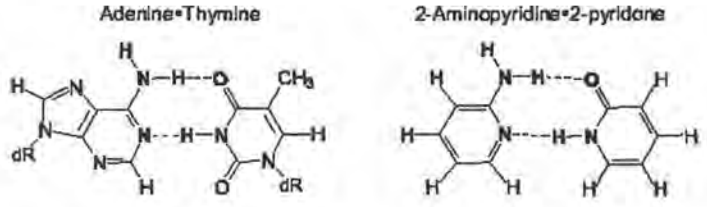


Figure 18: Analogy of 2-aminopyridine·2-pyridone to adenine·uracil.

analogues [6-8]. Our current focus is on 2-aminopyridine·2-pyridone as a direct analogue of adenine·uracil [8] (see Figure 18), and on the ground and excited state double proton transfer processes in 2-hydroxypyridine·2-pyridone, which gives rise to tunneling splittings [9].

- *Subproject D:*
  The $C_4H \cdot H_2O$ complex is important for astrochemistry and cometary chemistry. The global and local minimum structures were studied with multi-configuration self-consistent field (MC-SCF) and second-order multi-reference perturbation theory (CASPT2). We are also calculating the lowest-lying excited states, which can be excited in the near IR.
- *Other project work*
  We performed an extensive ab initio theoretical study of five low-energy isomers of the water hexamer (Chair, Cage(du)[1], Book, Prism, and Boat), their intramolecular vibrations, binding energies $D_e$ and dissociation energies $D_0$. Møller-Plesset second order perturbation calculations using the aug-cc-pVTZ basis set at aug-cc-pVDZ optimized geometries including vibrational zero point energy (ZPE) corrections predict Chair to be the most stable isomer, followed closely by Cage(du)[1] (+0.02 kcal/mol) and Book (+0.05 kcal/mol), while Prism is 0.15 kcal/mol higher [10]. Very recently, we extended to a study of the large-amplitude flipping vibrations of the Cage hexamer, which exhibit double-minimum potentials [11].

**References**

[1] M. Meuwly, A. Bach, and S. Leutwyler, J. Am. Chem. Soc., **123**, 11446 (2001).

[2] A. Bach, C. Tanner, C. Manca, H.-M. Frey and S. Leutwyler, J. Chem. Phys., in print (2003).

[3] D. Henseler, C. Tanner, H.-M. Frey, and S. Leutwyler, J. Chem. Phys. **115**, 4055 (2001).

[4] C. Wickleder, D. Henseler, and S. Leutwyler, J. Chem. Phys.**116**, 1850 (2002).

[5] C. Tanner, D. Henseler, S. Leutwyler, L. L. Connell, and P. M. Felker, J. Chem. Phys. **118**, 9157 (2003).

[6] A. Müller, F. Talbot, and S. Leutwyler, J. Chem. Phys. **115**, 5192 (2001).

[7] A. Müller, F. Talbot, and S. Leutwyler, J. Chem. Phys. **116**, 2836 (2002).

[8] A. Müller, F. Talbot, and S. Leutwyler, J. Am. Chem. Soc. **124**, 14486 (2002).

[9] D. R. Borst, J. R. Roscioli, D. W. Pratt, G. M. Florio, T. S. Zwier, A. Müller, and S. Leutwyler, Chem. Phys. **283**, 341 (2002).

[10] M. Losada and S. Leutwyler, J. Chem. Phys. **117**, 2003 (2002).

[11] M. Losada and S. Leutwyler, J. Chem. Phys., in print (2003).

**Project title:** Aerodynamic investigation and visualization analysis of vortex evolution for high speed delta wing type lifting bodies

**Project leader:** P. Leyland[1]

**Researchers:** J. Favre[2]
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**Institutions:** [1]Institut des Sciences de l'Energie, EPF-Lausanne
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[3]SMR SA, Bienne

**Description**

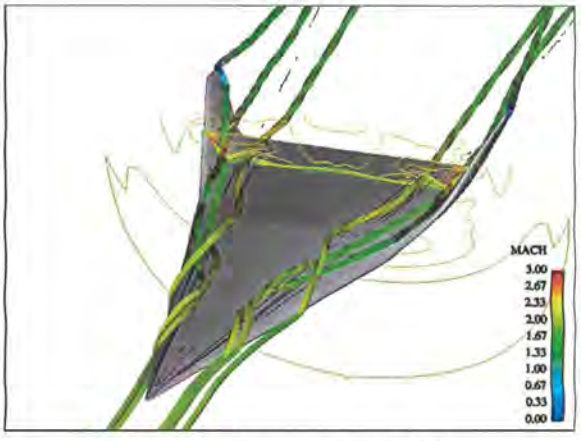
This work concerned the investigation of the flight capabilities and physical flowfield characteristics of high speed flow in supersonic and hypersonic regimes over a delta wing configuration with winglets, destined to be the first stage of a two stage to orbit reusable launcher system. Comparisons were made with experiments at RWTH-Aachen where extensive visualization techniques, like Schlieren photography, vapor screen light sheets combined with PIV, and oil flow patterns were obtained. These are backed up by surface pressure and heat flux measurements which can be used to validate the simulations. Visualization of the simulated flowfield brings insight into the vortical structures.

The first stage of a TSTO configuration which is destined to fly up to medium altitude, approximately 30 km, and then to launch an orbital second stage has been designed. The geometry is composed of a rounded leading edge delta wing with winglets. Delta wings are used for supersonic and hypersonic flow for their increased vortical lift and maneuverability given by the development of the vortex sheets over the leeward side of the wing. Investigations of the aerodynamic behavior and the flowfield characteristics obtained both by experimental means at RWTH-Aachen and by numerical simulations performed by EPFL on the NEC SX5 at CSCS, Manno, were made. The physics of the flowfields are investigated via the visualization techniques of experimental means (oil-flow, vapor screen techniques, laser sheet and PIV) and computational (extracted vortex techniques from visualization packages, computed skin-friction and streamline distributions, pressure distributions), in collaboration with the CSCS and SMR, Bienne. Precise scientific visualization is an integral part of the analysis of numerical simulations.

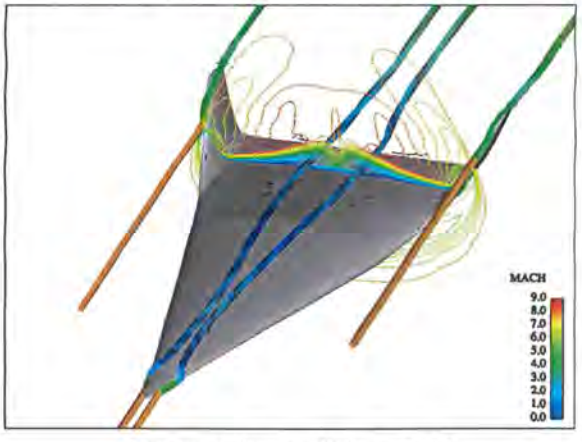
- *Visualization techniques*
  Post-processing, or ideally, interactive processing of simulation in computational sciences has progressed significantly over the last 15 years. Many academical, institutional and non commercial packages offer these capabilities. The list is long. For the engineer, although colored fluid dynamics is of great interest for studying the physics and detect eventual anomalies due to the numerics, the underlying discretization grid, the flow conditions, or producing images for presentations, the most important part remains the extraction of the aerodynamic coefficients from the calculation database, and the evolution of key parameters along specific lines, often corresponding to experimental or flight data. The extraction becomes automatic within most commercial packages where the integrated environment automatically renders such data, as well as providing integrated colored visualization capabilities. There still remains the question of how much confidence one may have in the rendered results and the precision of the visualization, when the whole process remains a black box. However, in aerothermodynamics, in-house codes still have a long life in front of them, as the developer can monitor specific methodology, and maintain a confidence limit for the results due to the intrinsic knowledge of what is done inside. One of the bottlenecks in post-processing is the need to rapidly manipulate large data

sets, typically several million computational cells, which is typical for aerospace applications. The setting up of the general view and the rapid execution of standard "scenes" like general flowfield in the volume projected onto the symmetry plane, the global pressure distribution on the wing, and the possibility of rapidly rotating in space the object and solution in order to detect the most pertinent views, particular phenomena or problems, can be extremely slow. Another question mark on the rendering of the solution, is the approximation made behind to render the visualization - interpolation level, integration scheme for the representation of streamlines, vortex core capabilities. The Graphical User Interface (GUI) is also important to be transparent and easy to understand [9]. Two graphical post-processing packages were used here, as both contain high level integration techniques for the representation of data. One is a commercial software EnSight [1] which presents a complete level of data analysis tools, with the particularity of rendering vortex core evolution, which is important for the application here, where the vortex topology is one of the main interests. The other, Baspl++ [2] is part of an integrated software for computational solid mechanics (CSM), and works with an underlying database system, Memcom2 which allows very fast access and manipulation of large data sets. This is due essentially to the design of the format and structure of the database, which is optimized for simulation data. Baspl++ is written in Python, an object-oriented (OO) scripting language. The classes for post-processing and visualization are implemented in C++ and interfaced to Python. The program is extensible; the user can write his own scripts giving access to all functionalities or use plug-ins which provide extensions. Since Baspl++ is fully OO, display and manipulation of multiple models and parts in several scenes is possible. EnSight can also access the Memcom database due to a user-defined reader library developed at CSCS. The visualization rendering for both packages are based on high level integration techniques. For example, in Baspl++ streamlines and field lines such as surface skin friction, the time integration is achieved by an element of fourth order (Runge Kutta - RK) integration in time, and an octree search for nearest neighbours. Specific integration depends on element type, hexahedra, tetrahedra together with their associated skewness factor. The EnSight particle trace algorithm integrates the vector flow field over time using also a RK method with a time varying integration step. Several integration parameters can be changed by the user. EnSight creates vortex core segments from the velocity gradient tensor of the 3D flow field. Core segments can then be used to place emitters for ribbon traces to help visualize the strength and nature of the vortices's. For streamlines integrations we usually do forward and backward integration from a cursor constrained to lie on the identified vortex cores. Currently, vortex cores are calculated according to two algorithms based on techniques outlined in [3-7]. Both techniques are linear and nodal. That is, they are based on decomposing finite elements into tetrahedrons and then solving closed-form equations to determine the velocity gradient tensor values at the nodes. The eigen-analysis algorithm uses classification of eigen-values and vectors to determine whether the vortex core intersects any faces of the decomposed tetrahedron. The vorticity based algorithm exploits the alignment of the vorticity and the velocity vectors to determine core intersection points. For data analysis extraction, such as aerodynamic coefficients, heat transfer coefficients, field distribution in particular points etc., the Memcom-Baspl system has several small tools such as an associated extractor which acts directly on the Memcom database.

- *Physics, Results and Figures*
  The two test cases retained here came from the FLOWNET network [8]. They correspond to a series of experiments at the AIA-RWTH supersonic wind tunnel, for $Mach_\infty = 2.0$, $\alpha = 0$–$10°$, and another in the hypersonic regime which was tested in the facilities of TH2 at the SWL-RWTH, $Mach_\infty \approx 7.7$. The two flow regimes are laminar and have similar characteristics concerning vortex formation. Their positioning and lift are different. In the supersonic case, the




Supersonic conditions AIA




Hypersonic conditions TH2

Figure 19: Vortex cores for supersonic case showing primary, secondary and tertiary vortices's, together with Mach isolines in a cross section plane at $x/L = 0.9$ (top); Comparison with the hypersonic conditions (below) showing the thicker roll-up of the shear layer closer to the body.

flow separates near the leading edge of the delta wing and progressively rolls up to a dominating vortex. A zone of separated flow can be seen in winglet region, with a zone of reattachment, and also separation and leading edge separation shock on the winglet. In the hypersonic case the thick boundary layer is part of the viscous shock layer which extends from the body to the outer bow shock, and provides strong viscous effects. These can be quite spectacular to visualize. The free shear layer again rolls up into a primary vortex which is larger, closer to the body, and closer to the centerline than for the supersonic case. For both cases primary separation and reattachment zones can be observed in the oil flow patterns, and the corresponding simulations. The roll-up of the boundary layer is clearly visible in both the supersonic and hypersonic cases, and can be represented by consecutive cross sections along the ELAC body. The vortex cores in Figure 19 are obtained by automatic extraction with Ensight followed by positioning streamlines along the core positions. Complete details of the analysis can be found in [8,9]. All the computations shown here were performed with the NSMB code on one or two processors of the SX-5 at Manno. Each calculation (specific Mach, angle of attack) took between 4 to 11 hours on one processor for computational grids of approximately 3 million cells, depending on the convergence difficulties due to the underlying physics. Comparisons with another similar code,

for the concerns of the numerical method, was performed on the Origin 3600 at EPFL on 16 processors, and gave the same physical results.

**References**

[1] CEI http://www.ensight.com

[2] MEMCOM 7, Baspl++. http://www.smr.ch; SMR Bienne (2002).

[3] D. Sujudi and R. Haimes, AIAA-95-1715 (1995).

[4] D. Kenwright and R. Haimes, IEEE Visualization **97** (1997).

[5] M. Roth and R. Peikert, IEEE Visualization **98** (1998).

[6] R. Haimes and D. Kenwright, AIAA-99-3288 (1999).

[7] R. Haimes and D. Kenwright, Massachusetts Institute of Technology (2000).

[8] P. Leyland and A. Perez and X. Pérusset, FLOWNET Final Report. Internal Report, EPFL (2002).

[9] P. Leyland, J. Favre, S. Merazzi, H. Olivier, and A. Henze, in *Proc. HESFF2 International Conference*, Marseille (2002).

**Project title:** Large eddy simulation of turbulence for interface tracking-based simulation of multi-phase flows

**Project leader:** P. Liovic

**Researchers:** D. Lakehal

**Institutions:** Nuclear Engineering Laboratory, ETH Zurich

### Description

In the short time access to CSCS resources has been available, porting of the MPI-based MFVOF-3D code to the IBM SP4 supercomputer has been successful. Initial runs using 16 CPUs have provided valuable insights into the nature of turbulence in bubbly flows, as well as the difficulties in quantifying turbulence in bubbly flow simulations. Studies using different LES subgrid-scale turbulence models are proceeding. With parallelism facilitated by domain decomposition, current speed-up with progressive increases in CPU count are in the order of 1.9. Other physics will be added in related projects in the near future.

In the other strand of this project, we have had recent success in porting the MPLES code to the IBM SP4 supercomputer. Apart from multi-fluid flow solver testing, the performance of the code is being tested on single SMP nodes of the IBM SP4. The implementing of OpenMP-based parallelization throughout this already highly vectorized code is under way. MPI-supported domain decomposition-based parallelism also already exists in the code.

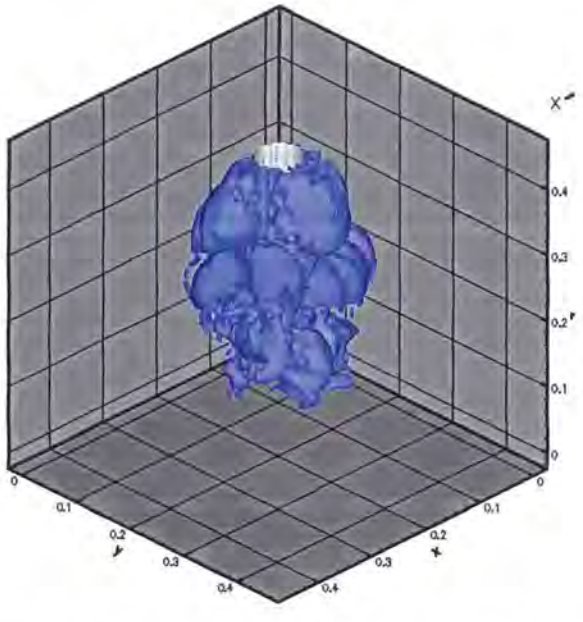



Figure 20: A snapshot of the bubbling resulting from gas venting from a downcomer pipe in a liquid bath. Inter-facial loci are captured using the Volume-of-Fluid (VOF) method.

**Project title:** Quantum chemical investigations of cyclization reactions involving cationic species

**Project leader:** J. Mareda

**Researchers:** C. Fouillet
J.-F. Fuchs
C. Chiancon
M. Rizello

**Institutions:** Organic Chemistry, University of Geneva

**Description**

Within this project the behavior and properties of the cationic species in presence of explicit solvent molecules were modeled with the quantum methods. 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 study of interactions between the reactive intermediates and the solvent molecules within the first solvation shell since they are treated explicitly. Our research indicate 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 are involved.

The mechanism of cation-olefin cyclization is also under investigation *via* model calculations for the *cis*-5,6-dimethyl-5-hexenyl cation by means of both *ab initio* and density functional theory methods. This type of cyclization is an important process in biosynthesis of many natural compounds. The cyclization of an appropriate substrate occurs either under solvolytic conditions or catalyzed by antibody. Our aim was also to improve the modeling for these reactions by sim-

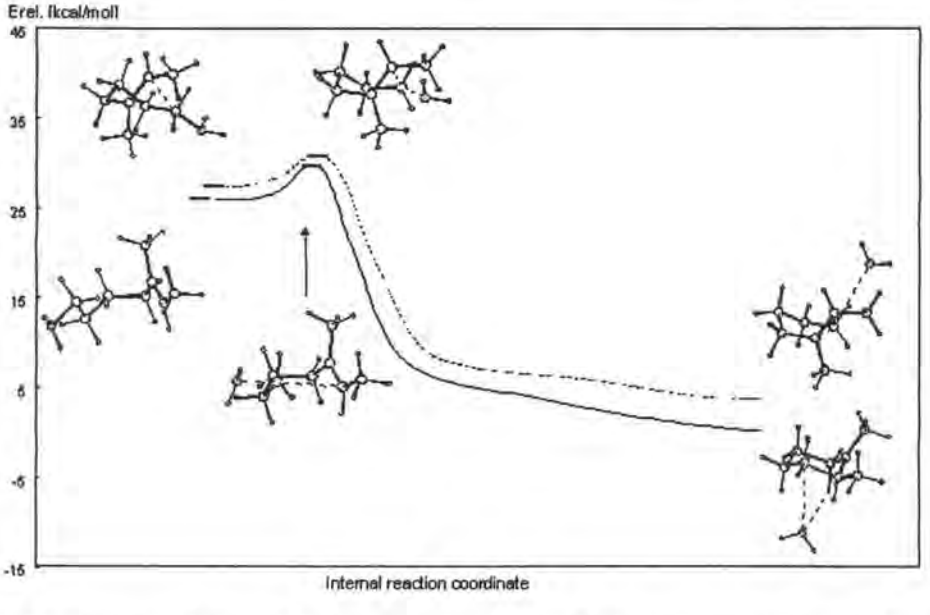



Figure 21: The computed potential energy surface along the intrinsic reaction coordinate for cyclizations of protonated *cis*-5,6-dimethyl-5-hexenol *via* the chair and the boat-like pathways, respectively.

ulating the leaving group by the removal of a neutral water molecule from the protonated *cis*-5,6-dimethyl-5-hexenol. At the highest level of approximation (MP4(SDQ)), the cation-olefin cyclization *via* chair-like pathway is slightly favored over the boat-like reaction path which leads to the protonated cyclopropane cation-water complex. Our work also shed light on the origin and mechanism by which the facial selectivity, albeit a weak one, occurs during the cyclization step. In order to appreciate the substitute effects in selectivity of cation-olefin cyclization, we also investigate the reaction where the reactant is substituted at C3 position with the −CPhMe2 and −SiPhMe2 groups. In case of uncatalyzed cyclizations the (-facial selectivity of the olefinic moiety remains, however, quite low. By characterization of cationic intermediates as well as the key transition states, this work provides an in depth understanding of the mechanism of cation-olefin cyclizations in solvolytic conditions. At present, we also extend our modeling to antibody catalyzed cation-olefin cyclizations, where an amazing selectivity is observed. The docking of an *ab initio* optimized stationary points show that (-carbocation interactions at the active site decrease very effectively and selectively the activation energy, leading to the virtually barrier-less collapse. Based on our computations we can provide a mechanistic explanation of these reactions, where in the presence of the antibody, the activation barrier leading to the observed product with (1*S*)(2*S*) configuration is selectively suppressed.

**References**

[1] J.-L. M. Abboud, O. Castaño, M. Herreros, J. Lomas, J. Mareda, P. Müller, R. Notario, and J.-C. Rossier, J. Org. Chem. **64**, 6401 (1999).

[2] C. Eder, C. Piguet, G. Bernardinelli, J. Mareda, C. G. Bochet, J. C. G. Bünzli, and G. Hopfgartner, Inorg. Chem., **39**, 5059 (2000).

[3] C. C. J. Fouillet, J. Mareda, J. Mol. Struct. Theochem **589**, 7 (2002).

[4] J. Lacour, D. Monchaud, J. Mareda, F. Favarger, and G. Bernardinelli, Helv. Chim. Acta., accepted for publication (2002).

**Project title:** Computational solid state physics

**Project leader:** P. F. Meier[1]

**Researchers:** E. P. Stoll[1]
T. A. Claxton[2]

**Institutions:** [1]Physics Institute, University of Zurich
[2]Department of Chemistry, University of York

**Description**

The electronic structures of $La_2CuO_4$ and $YBa_2Cu_3O_7$ have been studied by first-principles cluster calculations before and after doping. Clusters containing up to five planar copper atoms were investigated using the density functional method. At variance with band-structure calculations, we have been able to determine the charge and spin distributions from molecular orbitals (MO) expressed as linear combinations of atomic orbitals (AO) localised at the nuclear sites. Doping is achieved by adding or subtracting an electron from the cluster which, although there is a change of spin state, produces a charge distribution which is remarkably similar to the charge distribution of the peripheral charge method which does not involve changes in spin state. The peripheral charge method is designed to simulate doping by placing a carefully chosen set of point charges beyond the periphery of the cluster and relies on the supposition that the hole distribution is closely related to the charge distribution. After analyzing the important occupied and unoccupied MO, along with the corresponding contributions of the AO in detail, it is shown that charge distributions alone cannot provide the details of the hole density. In $La_2CuO_4$ the "intrinsic holes" are 65% localised on the copper cations, the rest are mainly located on the planar oxygen anions. This interpretation also explains the previously unnoticed significance of the 0.5 electrons occupancy of the copper $4s$ orbital, which is found in all clusters studied here. However the peripheral charge method enables charge distribution changes to be obtained for fractional changes in doping. For example the loss of charge initially depopulates the $3d_{x^2-y^2}$ and $2p_\sigma$ orbitals after which the charge extraction is less selective. This redistribution of charges influences the electric field gradients and hyperfine coupling parameters and could lead to structural changes. The theoretical values for the field gradients are compared to experiments.

**References**

[1] S. Renold, T. Heine, J. Weber, and P. F. Meier, Phys. Rev. B., submitted.

[2] S. Renold, S. Pliberšek, E. P. Stoll, T. A. Claxton, and P. F. Meier, Eur. Phys. J. B **23**, 3 (2001).

[3] P. F. Meier, Physica C **364-365**, 411 (2001).

[4] T. Mayer, diploma thesis, University of Zurich (2002).

[5] H. U. Suter, E. P. Stoll, and P. F. Meier, Physica B, in print (2002).

[6] E. P. Stoll, T. A. Claxton, and P. F. Meier, Phys. Rev. B **65**, 64532-1 (2002).

[7] S. Pliberšek, PhD thesis, University of Zurich (2001).

[8] S. Renold and P. F. Meier, Journal of Superconductivity, submitted.

[9] E. P. Stoll, T. A. Claxton, and P. F. Meier, Eur. J. Phys. B, submitted.

[10] C. Bersier, E. P. Stoll, P. F. Meier, and T. A. Claxton, Journal of Superconductivity: Incorporating Novel Magnetism, **15**, 399 (2002).

**Project title:** Global climate change: modeling atmosphere/ocean variability on decadal time scales

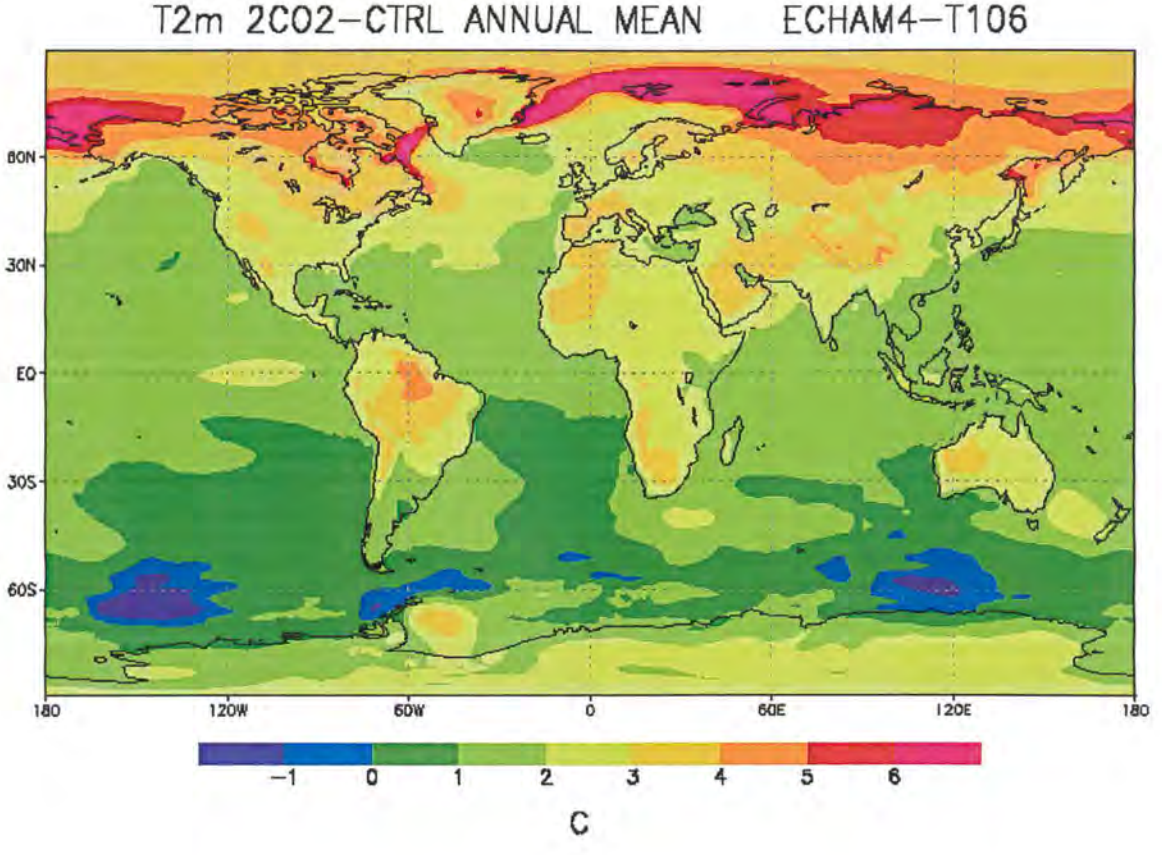
**Project leader:** A. Ohmura

**Researchers:** M. Wild

**Institutions:** Institute for Atmospheric and Climate Science, ETH Zurich

## Description

As one part of the Swiss NCCR-Climate program, the coupled ocean-atmosphere model HOPE/-ECHAM5 is used to study the natural climate variability and its perturbation due to humans. HOPE/ECHAM5 is the current version of the Max-Planck-Institute for Meteorology, Hamburg, climate model. At CSCS we perform predictability experiments of the Monte-Carlo type to assess the dependence of climate variables on the initial conditions of the thermohaline circulation (6 ensemble members of 20 years for two different ocean initial conditions finished). Furthermore, a scenario calculation for the 21st Century with 1% CO2-increase is done to complement similar runs performed elsewhere (underway). The focus of the evaluation of our group are energy fluxes, snow pack, and the climatic future of Europe, Greenland and Antarctica.




## References

[1] M. Wild, in *Intergovernmental Panel on Climate Change (IPCC), IPCC third assessment report* (Cambridge University Press, 2001), p. 944.

[2] A. Roesch, M. Wild, H. Gilgen, and A. Ohmura, Climate Dynamics **17**, 933 (2001).

[3] C. Schneeberger, O. Albrecht, H. Blatter, M. Wild, and R. Hoeck, Climate Dynamics **17**, 825 (2001).

[4] R. Van de Wal, M. Wild, and J. de Wolde, Tellus **53B**, 94 (2001).

[5] R. Van de Wal and M. Wild, Climate Dynamics **18**, 359 (2001).

[6] M. Wild, A. Ohmura, H. Gilgen, J. J. Morcrette, and A. Slingo, J. Climate **14**, 3227 (2001).

[7] M. Wild and R. Cechet, Tellus **54A**, 330 (2002).

[8] M. Wild, P. Calanca, S. Scherrer, and A. Ohmura, J. Geophys. Res., in press (2002).

**Project title:** Disordered network-forming materials

**Project leader:** A. Pasquarello[1]

**Researchers:** A. Bongiorno[1]
L. Giacomazzi[1]
F. Giustino[1]
P. Umari[1]
Z. Sljivancanin[1]
V. Dubois[1]
T. Oda[1]
C. Massobrio[2]
G.-M. Rignanese[3]
A. Stirling[4]
M. Verstraete[3]

**Institutions:** [1]Faculty of Basic Sciences, IRRMA, EPF Lausanne
[2]Strasbourg
[3]Louvain
[4]CSCS, ETH Zurich

**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 sub-projects:

1. *Vitreous materials*
   Modeling approaches are developed in order to extract detailed information regarding the structure of network-forming glasses from experimental data (e.g. $SiO_2$, $B_2O_3$, $GeSe_2$). More specifically, one of the goals is to implement a tool based on density functional theory in order to reproduce Raman spectra for such materials.
2. *Thin dielectric films on silicon*
   With the continuously reducing dimensions of electronic devices, there is a growing demand for an understanding of the properties of the Si-$SiO_2$ interface at the atomic scale. One of the main goals consists in providing an atomistic description of the mechanisms which govern the oxidation process and which lead to the formation of the Si-$SiO_2$ interface.
3. *Aqueous systems*
   First-principles molecular dynamics are used to investigate the structural and dynamical properties of the hydration of transition metal ions, for which an important interplay between structural and electronic properties occurs. The long-term challenge is to address electronic processes in chemical and biological systems.

**Achievements**

During the elapsed year, major results were obtained in the first two research directions of the project: (1) vitreous materials, (2) thin dielectric films on silicon. The third direction, (3) structure and dynamics of hydrated ions, has suffered from the difficulty of finding a post-doctoral researcher, which only joined our group on 1st October 2002 (Dr. V. Dubois). No particular progress will therefore be reported on the latter research direction in the following. We will instead report on the secondary project *Bio-inspired ammonia synthesis by catalysis on nanostructured surfaces*

started on 1st January 2002.

1. *Vitreous Materials*

   - Having set up a computational tool for the calculation from first principles of the dielectric tensors of relatively large systems, we could turn to the physical systems of interest to us. We started by addressing the Raman spectrum of vitreous silica. To this end, we used a model structure which we used previously for calculating the vibrational spectra obtained by inelastic neutron scattering and infrared absorption. These two spectroscopies turned out to be mainly sensitive to the short range order which is represented by tetrahedral $SiO_4$ units. By contrast, the Raman spectrum shows a much larger sensitivity to the medium range order. This observation is very interesting and reveals that the Raman spectrum can be used to extract different structural properties of the glass than one can obtain from the other spectroscopies. In particular, we determined the Raman matrix element for O bending motions which are responsible for the largest part of the HH Raman spectrum. We found that these matrix elements show a close to linear dependence on the Si-O-Si angle. Using a specific sum rule on the intensities, we could then extract rather accurate estimates for the concentration of three- and four-membered ring structures. Our estimates are considerably lower than the concentrations found by classical molecular dynamics, which probably still suffer from too high cooling rates. Finally, we undertook the same detailed study for the glass $B_2O_3$ (see Figure 22). This effort is still in progress. In collaboration with P. Umari

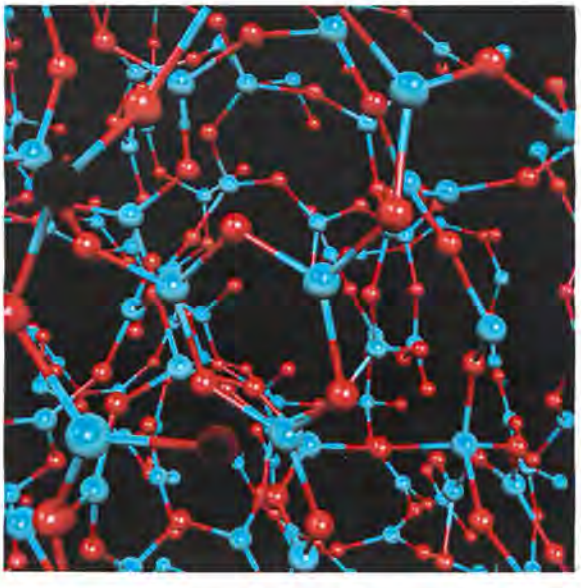


Figure 22: Model of vitreous $B_2O_3$.

   (IRRMA) and X. Gonze (Louvain-La-Neuve) [6,18,26].

   - A second major result achieved during the elapsed year is methodological. In the search for an efficient way of calculating dielectric constants from first principles, we realized that it was possible to apply a *finite* homogeneous electric field within a simulation cell satisfying periodic boundary conditions. This result could be achieved within the framework of the modern theory of polarization. The nonperiodic and unbound nature of the electric field potential generally prevents the application of a finite field within a periodic system. Overcoming this difficulty, allowed us to derive dielectric constants, both low- and high-frequency ones, from calculations of the polarization by taking finite differences. In partic-

ular, for evaluations of static dielectric constants, this method completely avoids the explicit calculation of the vibrational modes offering a scheme of great potential for studying systems of large size. These ideas have been implemented in the context of *ab initio* molecular dynamics and will allow us to study the evolution of the structural and dielectric properties of liquid systems under the application of an electric field. In collaboration with P. Umari (IRRMA) [10].

- We studied paramagnetic Si dangling-bond defects in vitreous silica. In particular, we focused on defect centers containing a $^{\bullet}Si{\equiv}SiO_2$ core unit. We showed that the hyperfine spectrum of this particular defect shows very good agreement with the experimental hyperfine spectrum of the *S* center. We could in this way assign the ESR line of the *S* defect to a particular atomic configuration. In collaboration with A. Stirling (Manno) [21].

2. *Thin dielectric films on silicon*
   - We refined our results on the diffusion of oxygen through a disordered oxide matrix. In particular, we investigated the effect of a denser $SiO_2$ layer close to the Si substrate on the oxidation rate. In collaboration with A. Bongiorno (IRRMA). An abstract concerning this work was accepted for oral presentation at the 26th International Conference on the Physics of Semiconductors, July 29 – August 2, 2002, Edinburgh [8,12,17,20].
   - In an effort to determine the bonding properties at the Si(100)-$SiO_2$ interface, we undertook a modeling effort in order to properly interpret experimental data obtained by Rutherford ion scattering in the channeling geometry. This type of measurement characterizes the bond pattern at the Si(100)-$SiO_2$ interface through its sensitivity to excess Si atoms, which comprise Si atoms in intermediate oxidation states (suboxide) as well as substrate Si atoms displaced out of their regular bulk positions. However, it is difficult to extract the atomic structure directly from the experimental data. In collaboration with L. C. Feldman, who provided us with unpublished scattering data as a function of ion energy, we addressed the "inverse scattering" problem by performing ion-scattering simulations on candidate atomistic models of the Si(100)-$SiO_2$ interface. In our simulations, we used the realistic Si(100)-$SiO_2$ model interfaces (see Figure 23), which were generated by combining classical molecular

Figure 23: Model interface of the Si(100)-$SiO_2$ interface.

dynamics and first-principles structural relaxations. In particular, we considered two model structures differing in the termination of the silicon substrate. In the first model, the termination is abrupt and closely corresponds to that of an ideal Si lattice. In the second model, the termination presents a reconstruction extending over a single monolayer. Theoretical values of the amount of excess silicon for the two model interfaces were then compared to the experimental results. The experimental data show good agreement with the reconstructed interface of the second model, while the abrupt interface in the first model significantly underestimates the observed yield. Since the suboxide contribution is equal for the two models, the difference between the models originates from the displacements of substrate Si atoms. Our results therefore clearly favor structural models of the Si(100)-$SiO_2$ interface in which the substrate terminates with a single reconstructed silicon layer. In collaboration with A. Bongiorno (IRRMA), M.S. Hybertsen (Agere Systems, Bell Labs), and L. C. Feldman (Vanderbilt University). An abstract concerning this work was accepted for presentation at the 26th International Conference on the Physics of Semiconductors, July 29 – August 2, 2002, Edinburgh [11,16,27].

- Amorphous zircon silicate is expected to replace $SiO_2$ in future Si-based electronic devices, because of its higher dielectric constant. We obtained two interesting results. The first result concerns the behavior of the low- and high-frequency dielectric constants as a function of zircon concentration. On the basis of first-principles calculations for crystalline systems, we developed a microscopic model to understand the behavior of the dielectric constants in *disordered* zircon silicates. The second result concerns the dependence of the Si $2p$ shift on the Zr content in disordered zircon silicates. We showed that this relation is approximately linear. Hence, the measurement of the Si $2p$ shift provides a practical way to establish the composition of the dielectric film. An abstract concerning the latter work has been accepted for oral presentation at the 33rd IEEE Semiconductor Interface Specialists Conference to be held in San Diego (CA), December 5-7 (2002). In collaboration with G.-M. Rignanese, X. Gonze, F. Detraux (Louvain-La-Neuve), F. Giustino (IRRMA), A. Bongiorno (IRRMA) [9,23].

3. *Bio-inspired ammonia synthesis by catalysis on nanostructured surfaces*
The major focus so far has been the characterization of the magnetic and structural properties of small Fe clusters deposited on a MgO surface. This theoretical study is intended to support an experimental investigation which is carried out in parallel at EPFL. The deposition of Fe clusters on a MgO surface corresponds to a preliminary stage of the experimental project (see Figure 24). As far as our theoretical investigation is concerned, we have so far shown that the deposited clusters $Fe_n$ closely preserve their three-dimensional gas-phase structure. However, the magnetic moments of very small adsorbed clusters ($n \leq 5$) show significant reductions with respect to their gas-phase values. These reductions result from an intra-cluster charge rearrangement caused by the interaction with oxygen $2p$ orbitals of the MgO surface, rather than from structural deformations or charge transfer from the oxide surface. As the size of the clusters increases, the gas-phase magnetic moments are recovered. These preliminary results will be the object of a publication. The manuscript is still in preparation. In collaboration with Z. Sljivancanin (IRRMA).

4. *Noncollinear magnetism: Liquid oxygen*
During Dr. T. Oda's visit to IRRMA (EPFL) in the summer 2000 (two months), a special allocation of CSCS has supported a specific project on *Noncollinear Magnetism*. The major results are summarized here. We modeled liquid oxygen using *ab initio* molecular dynamics in which both the atomic structure and the noncollinear magnetic structure evolve without constraints.

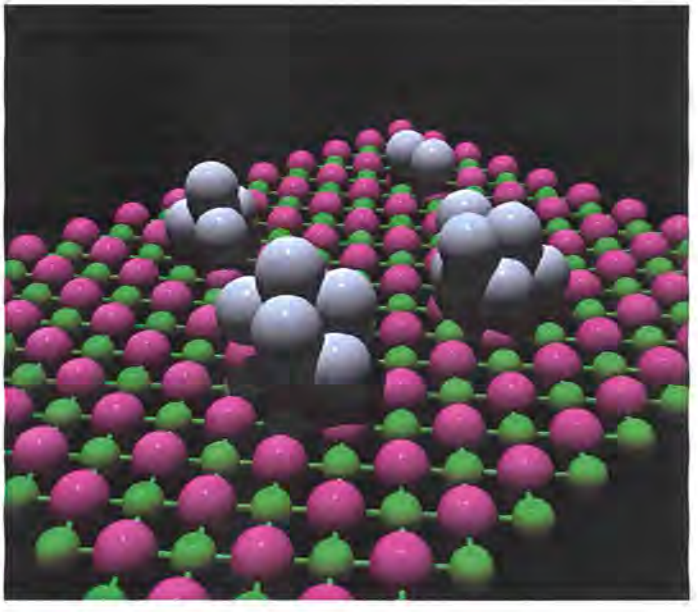


Figure 24: Small Fe clusters on a MgO(100) surface.

The atomic structure shows preference for parallel alignment of first-neighbor molecules and is supported by an excellent agreement between theoretical and experimental nuclear structure factors. The magnetic structure shows short-range antiferromagnetic correlations in agreement with spin-polarized neutron diffraction data. The observed correlations primarily result from appropriate trajectories of colliding $O_2$ molecules. The simulation provides evidence for the occurrence of long-living $O_4$ molecular units. In collaboration with T. Oda (Kanazawa) [13,22].

**References**

[1] A. Bongiorno and A. Pasquarello, Microelectronics Engineering **59**, 167 (2001).

[2] A. Pasquarello, Curr. Opin. Solid St. M. **5**, 503 (2001).

[3] R. Haerle, E. Riedo, A. Pasquarello, and A. Baldereschi, Phys. Rev. B **65**, 045101 (2002).

[4] A. Bongiorno and A. Pasquarello, Phys. Rev. Lett. **88**, 125901 (2002).

[5] A. Palma, A. Pasquarello, and R. Car, Phys. Rev. B **65**, 155314 (2002).

[6] P. Umari and A. Pasquarello, Physica B **316-317**, 572 (2002).

[7] G.-M. Rignanese and A. Pasquarello, in *Alternatives to $SiO_2$ as Gate Dielectric for Future Si-Based Microelectronics, Materials Research Society Workshop Series*, edited by J. Morais and I. J. R. Baumvol (2001), no. 24.

[8] A. Bongiorno and A. Pasquarello, in *Alternatives to $SiO_2$ as Gate Dielectric for Future Si-Based Microelectronics, Materials Research Society Workshop Series*, edited by J. Morais and I. J. R. Baumvol (2001), no. 31.

[9] G.-M. Rignanese, F. Detraux, X. Gonze, A. Bongiorno, and A. Pasquarello, Phys. Rev. Lett. **89**, 117601 (2002).

[10] P. Umari and A. Pasquarello, Phys. Rev. Lett. **89**, 157602 (2002).

[11] A. Bongiorno and A. Pasquarello, Materials Science and Engineering B **96**, 102 (2002).

[12] A. Bongiorno and A. Pasquarello, Solid State Electronics **46**, 1873 (2002).

[13] T. Oda and A. Pasquarello, Phys. Rev. Lett. **89**, 197204 (2002).

[14] A. Pasquarello, Journal de Physique, to appear.

[15] A. Pasquarello and R. Resta, in *Proceedings of the 12th Workshop on Fundamental Physics of Ferroelectrics*, Washington, D.C., February 3-6, accepted for publication (2002).

[16] A. Bongiorno, A. Pasquarello, M. S. Hybertsen, and L. C. Feldman, in *Proceedings of the 26th International Conference on the Physics of Semiconductors*, edited by A. Long and J. Davies (Institute of Physics, Bristol, 2002), to appear.

[17] A. Bongiorno and A. Pasquarello, in *Proceedings of the 26th International Conference on the Physics of Semiconductors*, edited by A. Long and J. Davies (Institute of Physics, Bristol, 2002), to appear.

[18] P. Umari and A. Pasquarello, Journal of Physics: Condensed Matter, accepted for publication.

[19] C. Massobrio, M. Celino, and A. Pasquarello, Journal of Physics: Condensed Matter, accepted for publication.

[20] A. Bongiorno and A. Pasquarello, Journal of Physics: Condensed Matter, accepted for publication.

[21] A. Stirling and A. Pasquarello, Phys. Rev. B, accepted for publication.

[22] T. Oda and A. Pasquarello, Journal of Physics: Condensed Matter, accepted for publication.

[23] F. Giustino, A. Bongiorno, and A. Pasquarello, Appl. Phys. Lett., accepted for publication.

[24] A. Trave, P. Tangney, S. Scandolo, A. Pasquarello, and R. Car, Phys. Rev. Lett., accepted for publication.

[25] A. Pasquarello and R. Resta, J. Chem. Phys., submitted.

[26] P. Umari, X. Gonze, and A. Pasquarello, Phys. Rev. Lett., submitted.

[27] A. Bongiorno, A. Pasquarello, M. S. Hybertsen, and L. C. Feldman, Phys. Rev. Lett., submitted.

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

**Project leader:** M. Posternak

**Researchers:** A. Baldereschi

**Institutions:** Institute of Theoretical Physics, EPF Lausanne

**Description**

Our activity during the past year has been focused on understanding and predicting from first-principles the structural and electronic properties of several different low–dimensional solid systems, including surfaces, interfaces, and nanostructures. In particular, we have carried on our work on the effect of surface morphology on the GaAs ionization potential, and examined the Ga-rich $\beta 2(4\times 2)$ and $\zeta(4\times 2)$ GaAs(001) surfaces. The results agree well with recent experiments, and the corresponding ionization-potential trends can be understood in terms of a model based on the electron counting rule. We have also completed our study on interface states in epitaxial Al/AlAs(001) junctions, and identified new resonant midgap interface states, not accounted for by commonly accepted models. These states correspond to intermetallic bonds between Al atoms of the semiconductor and those of the metal, and derive from surface states of the Al(001) and of the unreconstructed AlAs(001) surface. Finally, we have studied the behavior of the local work function around various low-index facet edges in Al and Na nanocrystals, and determined

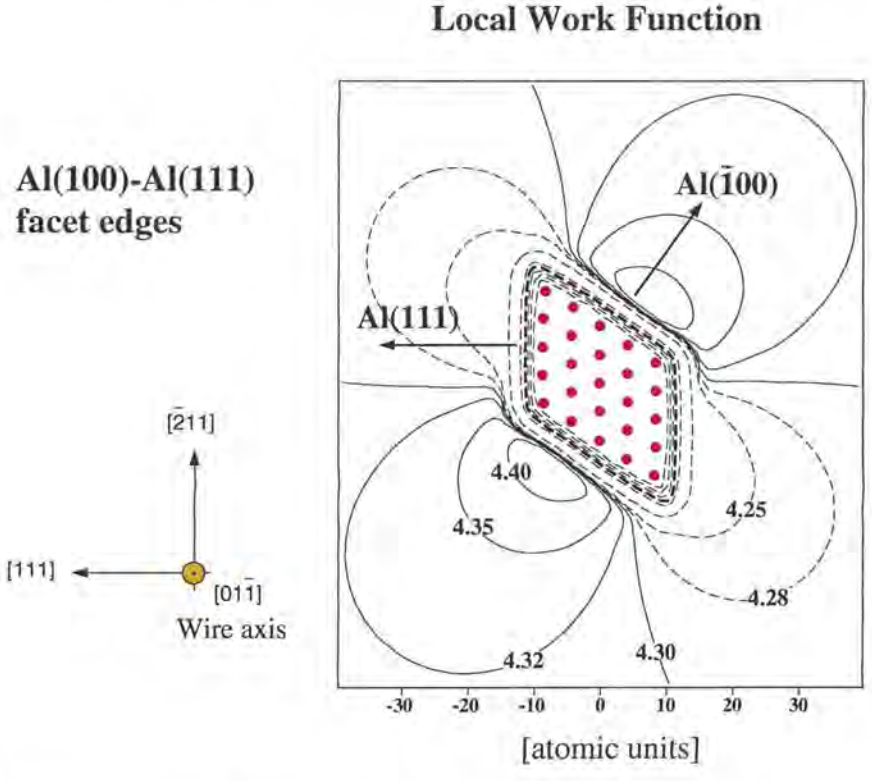



Figure 25: Contour plot of the local work function (in eV) around an aluminum nanowire containing facet edges between Al(100) and Al(111) surfaces. Continuous (dashed) lines indicate regions above (below) the work-function value at infinity. The red disks indicate Al atomic columns.

the microscopic mechanism which allows different work functions to coexist on different faces of a single crystal.

**References**

[1] C. J. Fall, N. Binggeli, and A. Baldereschi, Phys. Rev. B **65**, 45401-1/6 (2002).

[2] C. J. Fall, N. Binggeli, and A. Baldereschi, Phys. Rev. Lett. **88**, 156802-1/4 (2002).

[3] C. J. Fall, N. Binggeli, and A. Baldereschi, Phys. Rev. B **66**, 075405-1/10 (2002).

[4] T. Maxisch, A. Baldereschi, and N. Binggeli, Solid State Commun. **126**, 265-8 (2003).

[5] T. Maxisch, N. Binggeli, A. Baldereschi, Phys. Rev. B **67**, 125315-1/6 (2003).

**Project title:** Quantum simulations of molecules and molecular complexes

**Project leader:** M. Quack

**Researchers:** L. Oeltjen
J. Stohner

**Institutions:** Laboratory of Physical Chemistry, ETH Zurich

**Description**

High-Resolution Infrared Spectroscopy is an important tool for the investigation of molecules and molecular complexes. The understanding and interpretation of highly resolved ro-vibrational spectra is central in atmospheric chemistry and physics [1-6] and material sciences such as microelectronics and chemical vapor deposition [7]. A detailed understanding of spectra requires large computational efforts due to the high-dimensionality (large number of vibrational and rotational degrees of freedom) of the Schrödinger eigenvalue equation. We have developed tools to compute and analyse (ro)vibrational spectra of relatively large molecules up to the high overtone region (see [8,9], and references therein). CDBrClF serves as a prototype molecule to study fundamental symmetry violation in molecular spectroscopy [10]. We have investigated the influence of parity violation on (ro)vibrational frequencies and thermodynamic properties in chiral molecules [11-14]. We are now investigating the effect of multi-dimensional anharmonic coupling in the parity violating potential on frequency shifts. Therefore, we calculated a 4D parity violating potential

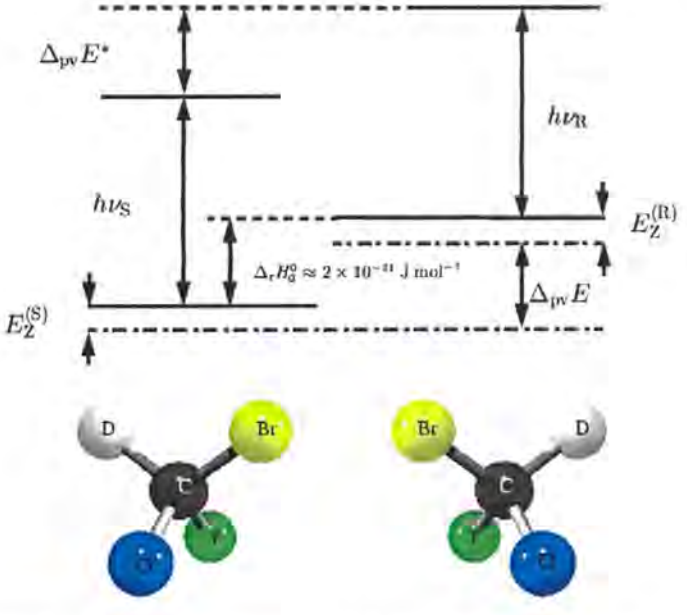



Figure 26: Energy levels scheme and geometry of bromochlorofluoromethane enantiomers. (S)-CDBrClF (left-hand side) is calculated to be lower in energy than (R)-CDBrClF with an enthalpy of stereomutation of about $\Delta_r H_0^0 \approx 20$ pJ mol$^{-1}$. The dash-dotted lines indicate the electronic potential energy minima including parity violating potentials, whereas the solid lines indicate vibrational (ground and excited state) levels including zero-point energy ($E_Z$) and parity violating corrections ($\Delta_{pv}E$, not to scale). The transitions to the dashed lines are forbidden, whereas transitions between the full lines are observable spectroscopically.

energy surface for CDBrClF [15], which is combined with the pure vibrational 4D potential energy surface [9] to achieve this goal.

**References**

[1] Y. He, H. Hollenstein, M. Quack, E. Richard, M. Snels, and H. Bürger, J. Chem. Phys. **116**, 974-983 (2002).

[2] G. S. Tschumper, M. L. Leiniger, B. C. Hoffmann, E. F. Valeev, H. F. Schaefer III, and M. Quack, J. Chem. Phys. **116**, 690-701 (2002).

[3] I. M. Mills and M. Quack, Mol. Phys. **100**, 9-10 (2002).

[4] M. Snels, H. Hollenstein, M. Quack, E. Cané, J. A. Miani, and A. Trombetti, Mol. Phys. **100**, 981-1001 (2002).

[5] M. Hippler and M. Quack, J. Chem. Phys. **116**, 6045-6055 (2002).

[6] G. D'Amico, M. Snels, H. Hollenstein, and M. Quack, Phys. Chem. Chem. Phys. **4**, 1531-1536 (2002).

[7] V. Boudon, M. Rotger, Y. He, H. Hollenstein, M. Quack, and U. Schmitt, J. Chem. Phys. **117**, 3196-3207 (2002).

[8] T.-K. Ha, M. Quack, and J. Stohner, Mol. Phys. **100**, 1797-1805 (2002).

[9] A. Beil, H. Hollenstein, O. Monti, M. Quack, and J. Stohner, J. Chem. Phys. **113**, 2701-2718 (2000).

[10] M. Quack, Angew. Chem. Int. Ed. (Engl.) **28**, 571 (1989) and **41**, 4618 (2002).

[11] R. Berger, M. Quack, and J. Stohner, Angew. Chem. Int. Ed. (Engl.) **40**, 1667 (2001).

[12] M. Gottselig, D. Luckhaus, M. Quack, J. Stohner, and M. Willeke, Helv. Chim. Acta **84**, 1846 (2001).

[13] R. Berger, M. Gottselig, M. Quack, and M. Willeke, Angew. Chem. Int. Ed. (Engl.) **40**, 4195 (2001).

[14] M. Quack and J. Stohner, CHIRALITY **13**, 745 (2001) and **15**, 375 (2003)

[15] M. Quack and J. Stohner, in preparation (2003) and Chimia **56**, 381 (2002).

**Project title:** Rational design of biomimetic compounds of galactose oxidase

**Project leader:** U. Röthlisberger

**Researchers:** L. Guidoni

**Institutions:** Inorganic Chemistry, ETHZ

**Description**

The copper enzyme Galactose Oxidase (GOase) oxidizes primary alcohols selectively to the corresponding aldehydes and is therefore of interest as a potential (stereo) selective, mild oxidation catalyst (Figures 27A and 27B). A parallel study of the enzyme and existing low-efficiency biomimetic compounds [1] based on mixed QM/MM Car-Parrinello simulations were recently carried out [2] and both systems were compared step by step throughout the catalytic cycle. The comparative study has identified that important discrepancies exist in the electronic structure of the transition state of the rate-determining step of the reaction. On the basis of these results, a –CH2 group was inserted to provide more flexibility and to break the extended conjugation (Figures 27C and 27D). This modification lowered by $\approx$ 5 kcal/mol the calculated activation energy barrier. We therefore designed a new class of computational models, where the binaphtyl moiety was substituted by a benzene ring and the axial ligand was omitted (Figure 27D). The copper-based models turned out to have, in the rate-determining step, geometrical and electronic properties similar to those of the larger functional synthetic compounds. Under experimental conditions the Cu-coordination is lost relatively easily. Searching for alternative transition metal reactive centers is therefore a crucial

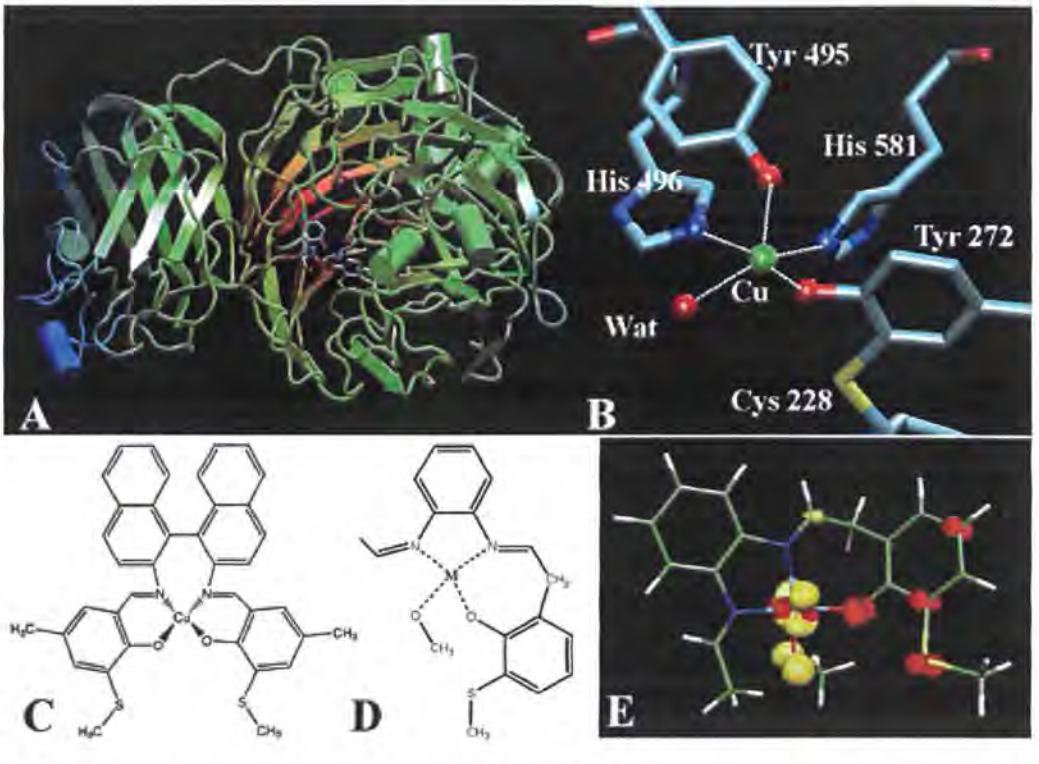



Figure 27: The copper enzyme galactose oxidase (GOase) (A) and its active site (B). Sketches of the functional biomimetic compound (C) [1] and of new designed biomimetic systems (D). Spin density contour (E) at the rate-determining transition state of compound (D) with M=Rh.

issue for designing more efficient catalysts. The DFT-based results show that rhodium is more tightly bound to the compound than copper, and the calculated activation barrier turned out to be competitive with that of the biomimetic of Stack (22.8 vs. 21 kcal/mol). Rhodium is therefore a good candidate as efficient catalytic centre. In contact with the experimental group of Prof. Grützmacher (Inorganic Chemistry, ETHZ) we are currently investigating modified biomimetic models having feasible synthetic strategies. These compounds are promising candidates to be successfully tested in experiments as efficient mild oxidation catalyst.

**References**

[1] Y. Wang, et al., Science **279**, 537 (1998).

[2] U. Röthlisberger et al., J. Biol. Inorg. Chem. **5**, 236 (2000).

[3] K. Spiegel and U. Röthlisberger, in preparation.

[4] M. C. Colombo, L. Guidoni, A. Laio, A. Magistrato, P. Maurer, S. Piana, U. Röhrig, K. Spiegel, M. Sulpizi, J. VandeVondele, M. Zumstein, and U. Röthlisberger, Chimia **56**, 13-19 (2002).

[5] L. Guidoni, P. Maurer, S. Piana, and U. Röthlisberger, QSAR, in press (2002).

[6] L. Guidoni and U. Röthlisberger, in preparation.

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

**Project leader:** U. Röthlisberger

**Researchers:** P. Maurer

**Institutions:** Institute of Molecular and Biological Chemistry, EPF Lausanne
Inorganic Chemistry, ETH Zurich

**Description**

In a first step of this project, we performed a detailed DFT study of the electron-induced dissociation of ethene from Re, Tc compounds complexed with 1,4,7-trithiacyclononane. These complexes are potential radiopharmaceuticals, and the availability of many experimental data for both product and reactant compounds makes these complexes an ideal test case to validate our computational approach. The structural agreement between experiment and calculations is overall excellent. No experimental data is available for reaction and activation energies, but our calculated values are consistent with experimental observations. In the second part, a mixed QM/MM approach is used to investigate the binding of radioactively labeled glucose derivatives to the enzyme Hexokinase I, which is a key target for radiopharmaceutical imaging agents. This enzyme consists of two almost identical domains, each containing 450 amino acids, and each binding to one molecule of glucose. Our classical MD simulations show that the two domains do not interact significantly on a nanosecond timescale so that it will be sufficient to simulate only one of the two domains in subsequent QM/MM binding studies of recently synthesized potential Tc radiopharmaceuticals to Hexokinase I. A reduction of the system size is of course highly desirable in view of the large size of the enzyme.

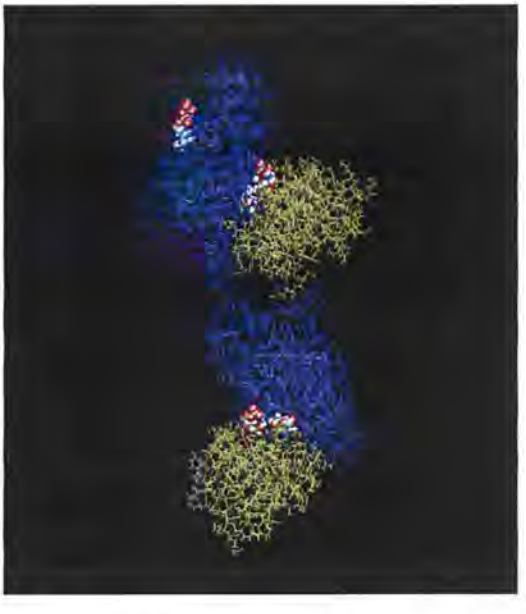


Figure 28: The enzyme Hexokinase I from human brain with the C-terminal half (catalytic) at the bottom and the N-terminal half (regulatory) on top. Each half consists of a large domain (blue) and a small domains (yellow). Both halves bind glucose and glucose-6-phosphate (shown in a space-filling representation) in the cleft between the large and small domain.

**References**

[1] L. Guidoni, P. Maurer, S. Piana, and U. Röthlisberger, Quant. Struct.-Act. Relat. **21**, 119 (2002).

[2] A. Magistrato, P. Maurer, T. Fässler, and U. Röthlisberger, J. Phys. Chem. A, accepted.

[3] P. Maurer, A. Magistrato, and U. Röthlisberger, in preparation.

**Project title:** Ab initio hybrid simulations of electron transfer reactions

**Project leader:** U. Röthlisberger[1]

**Researchers:** S. Piana[1]
M. Sulpizi[2]
A. Laio[3]

**Institutions:** [1]Laboratory of Computational Chemistry and Biochemistry, EPF Lausanne
[2]International School for Advanced Studies, Trieste
[3]Centro Svizzero di Calcolo Scientifico (CSCS), Manno

**Description**

Redox reactions and electron transfer (ET) processes are ubiquitous in Chemistry as well in Biology where they are involved in such crucial functions as respiration and photosynthesis. In this project, we use QM/MM Car-Parrinello simulations [1] to provide a detailed atomistic picture of adiabatic ET processes occurring in complex environments. To this end, we have developed a method to steer ET reactions along a global electronic reaction coordinate. The method is based on the calculation of dynamically-generated electrostatic potential derived point charges (D-RESP charges) [2] that allow to impose a restraining potential on the electronic charge distribution [3]. As a first test case, we investigated the electron transfer-induced dissociation of the para-cyanochlorobenzene anion in water, which has been extensively, characterized both from a theoretical and experimental point of view. Using a thermodynamic integration approach, our method is able to reproduce the free energy barrier of electron transfer-induced dissociation. It also permits a detailed analysis of the structural rearrangements of solute and solvent as the reaction proceeds. We believe that this method can find wide applications and extensions to other systems, in particular when the reaction is characterized by a highly multidimensional "traditional" geometric coordinate.

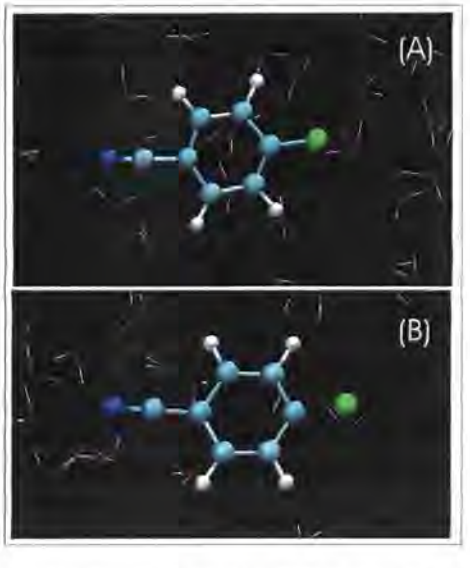



Figure 29: Para-cyanochlorobenzene anion in water: (A) bound form: (B) dissociated form. The QM solute is depicted in ball and sticks.

**References**

[1] A. Laio, J. VandeVondele, and U. Röthlisberger, J. Chem. Phys. **116**, 6941 (2002).

[2] A. Laio, J. VandeVondele, and U. Röthlisberger, J. Chem. Phys. B **106**, 7300 (2002).

[3] M. Sulpizi, A. Laio, J. VandeVondele, and U. Rothlisberger, in preparation.

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

**Project leader:** U. Röthlisberger

**Researchers:** U. F. Röhrig
M. C. Colombo
H. W. Hugosson

**Institutions:** Institute of Molecular and Biological Chemistry, 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. In order to address these challenging systems, and to determine the ability of our theoretical tools to describe them, we have started by carrying out comparative theoretical studies of nucleotide and nucleoside solvation in water. In these molecular dynamics simulations we use a range of theoretical methods, from purely classical force field simulations (AMBER), via a hybrid QM/MM scheme, to fully quantum mechanical calculations, within the Car-Parrinello molecular dynamics (using the CPMD program). Up to now, the classical simulations have been performed, while the QM/MM and the full QM simulations are still in production. The quality of the classical force field can be assessed and, where necessary, reparameterized in a direct force-matching procedure. Classical equilibration of the structure of one DNA repair enzyme, Endonuclease IV, is also in progress.

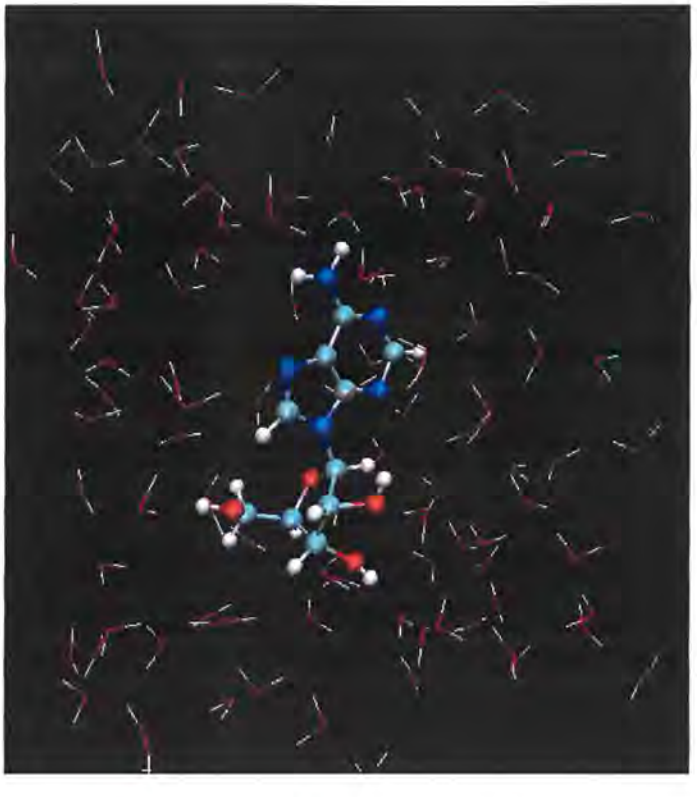


Figure 30: RNA adenosine solvated in water.

**References**

[1] K. Spiegel, U. Röthlisberger, and P. Carloni, in preparation.

[2] H. W. Hugosson, K. Spiegel, P. Carloni, and U. Röthlisberger, in preparation.

[3] A. Laio, J. VandeVondele, and U. Röthlisberger, J. Chem. Phys. **116**, 6941 (2002).

[4] A. Laio, J. VandeVondele, and U. Rothlisberger, J. Chem. Phys. B **106**, 7300 (2002).

[5] M. Sulpizi, A. Laio, J. VandeVondele, and U. Röthlisberger, in preparation.

**Project title:** Cloud-resolving numerical simulation of Alpine precipitation systems

**Project leader:** C. Schär

**Researchers:** O. Fuhrer
D. Lüthi
A. Walser

**Institutions:** Institute for Atmospheric and Climate Science, ETH Zurich

**Description**

The rapid increase in computer power will soon allow for atmospheric models with horizontal resolutions near 1 km for operational weather prediction purposes. It is expected that this will be particularly beneficial for the forecasting of convective cloud systems (thunderstorms). Due to the lack of appropriate resolution, such weather systems are currently parameterized. The use of cloud-resolving models raises, however, a wide range of physical and numerical questions. Here we address two particularly important issues:

- *Predictability of precipitation*
  The skill of numerical weather predictions (NWP) is intrinsically limited by the chaotic nature of the atmospheric dynamics. Small uncertainties in the initial conditions can rapidly grow and disrupt deterministic predictability. Useful deterministic forecasts are thus restricted to comparatively short lead times. In order to estimate the uncertainty of a single forecast, a series forecasts with slightly modified initial conditions can be employed. This method is referred to as ensemble prediction. Ensemble prediction systems are currently applied to medium-range (3-10 days) large-scale weather forecasting purposes. They can be used to estimate the predictability of the atmospheric state, and to provide probabilistic forecasts. There is much less experience, however, with short-term predictability at smaller scales, such as relevant in heavy precipitation events.

  In this study, we investigate the predictability of convective precipitation systems. To this end, 24-hours ensembles with up to 24 simulations are performed using the Canadian high-resolution NWP model MC2 over the European Alps (Figure 31). The simulations use a horizontal grid spacing of 3 km and 50 levels in the vertical. The simulations are conducted on the NEC SX5 at the Swiss Centre for Scientific Computing in Manno. One of these 24-hours simulations uses $\approx$ 17 CPU hours at 1.8 GFlops.

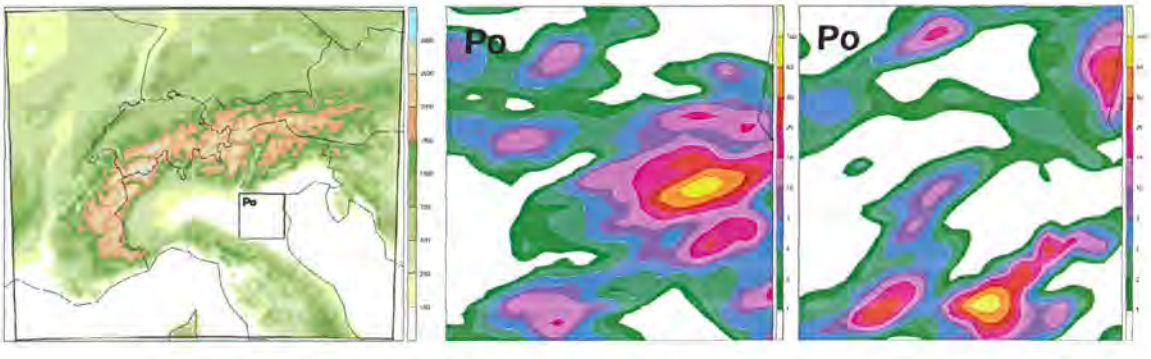



Figure 31: MC2 model domain with topography and 24 h accumulated precipitation [mm] in the eastern Po region for two ensemble simulations on July 29, 1999. The differences in the integrations pinpoint the large uncertainties for precipitation forecasting in this case.

Results suggest that the small-scale predictability of precipitation differs strongly from case to case, depending upon the weather type and the spatial and temporal scales considered (Walser et al. 2003). During episodes of convective activity, predictability limitations can be crucial even on the scales of large Alpine river catchments, thus strongly affecting runoff forecasts. Figure 31 illustrates the accumulated daily precipitation amounts for a 120 × 120 km sub-domain in the eastern Po valley. The two panels relate to two selected members of the ensemble, and the differences illustrate the large uncertainties of this particular weather event. Our research aims toward developing methodologies for probabilistic precipitation forecasting in such cases.

- *Dynamics of precipitation events*
  When a moist atmospheric airmass impinges on a mountain-ridge, it is forced to ascend, expand and cool. If the cooling is sufficient, some of the water vapor will condense and lead to the formation of clouds and precipitation. The associated latent heat release can cause buoyant updrafts that may grow into deep convective cells. It is the objective of our research to investigate the dynamical and physical properties of mountain-induced precipitation regimes as a function of the upstream flow profiles.

  For this purpose, we perform idealized three-dimensional simulations of a two-dimensional airstream interacting with a mountain ridge. The simulations are carried out on the NEC SX5, using a model domain of 490 km × 50 m with a gridspacing of 1 km. In the vertical 65 model levels with a spacing of 80 to 400 m are used. A relatively small timestep of 7 seconds is necessary since large vertical velocities occur in the center of the convective updrafts.

  Figure 32 shows a comparison of two simulations. In panels (a) the incoming flow is cold and not very moist, leading to a two-dimensional stationary cloud over the ridge with little precipitation. As the incoming flow in (b) is warmer and moister, strong convective cells evolve, travel over the mountain ridge, and decay to its lee. The symmetry of the two-dimensional flow geometry is broken and a three-dimensional convective circulation is established, associated with strong winds and heavy precipitation. Results show that the formation of convective rolls may significantly enhance precipitation over the topography. Ongoing research at our institute is geared toward identifying the various flow regimes that may result.

- *Climate modeling*
  Until recently, all our regional climate simulations have been conducted on the Cray SV1 of ETH Zurich. Currently we are working on the migration of these applications to the IBM and NEC systems in Manno. Most of the climate modeling activities will be shifted to Manno toward the end of this year.

**References**

[1] R. Benoit, C. Schär, P. Binder, S. Chamberland, H. C. Davies, M. Desgagné, C. Girard, C. Keil, N. Kouwen, D. Lüthi, D. Maric, E. Müller, P. Pellerin, J. Schmidli, F. Schubiger, C. Schwierz, M. Sprenger, A. Walser, S. Willemse, W. Yu, and E. Zala, Bull. Amer. Meteor. Soc. **83**, 85 (2002).

[2] C. Flamant, E. Richard, C. Schär, M. Sprenger, L. Nance, and R. Rotunno, Quart. J. Roy. Meteorol. Soc., submitted (2003).

[3] O. Fuhrer and C. Schär, in *Proc. 10th Conf. Mountain Meteorology*, Park City, American Meteorological Society, 198 (2002).

[4] K. Jasper, J. Gurtz, and H. Lang, J. Hydrol. **267**, 38 (2002).

[5] K. Jasper, J. Gurtz, and H. Lang, Hydrol. Earth Sys. Sci., in press (2003).

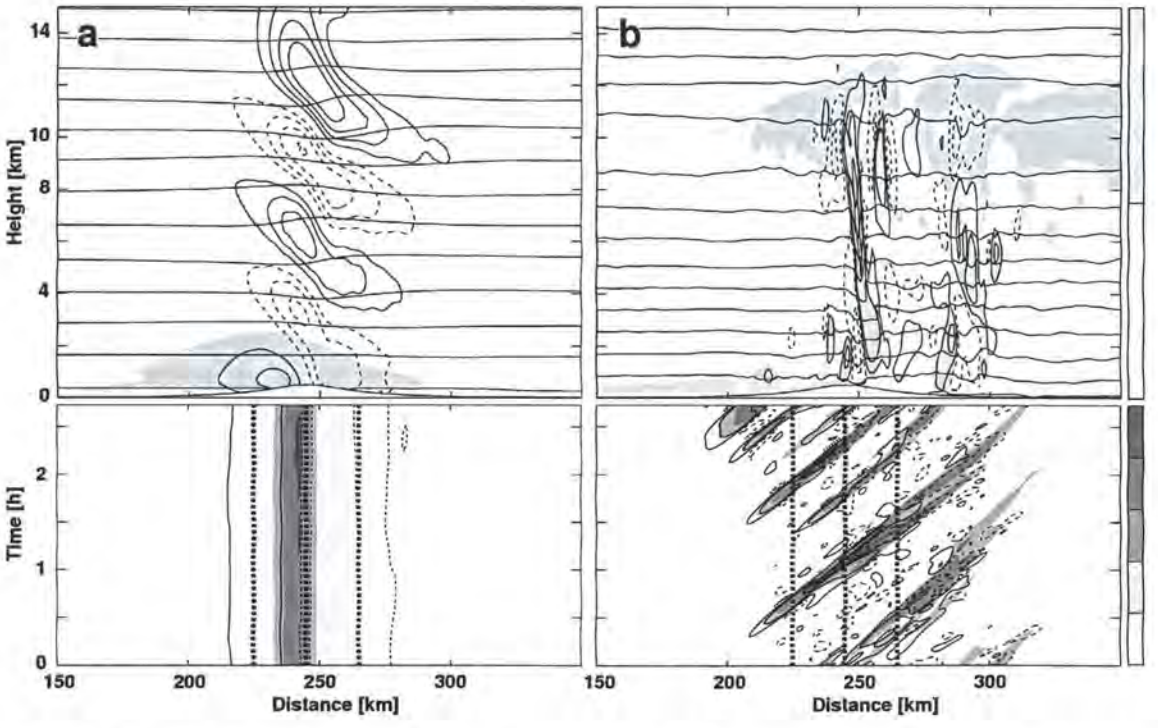



Figure 32: Idealized simulations of three-dimensional moist flow past a two-dimensional mountain ridge. Upper panels show xz-sections after one day of integration, with vertical velocity (thin contours), potential temperature (contours every 4 K) and clouds (light shading). Lower panels show xt-diagrams close to the surface with vertical velocity (thin contours), precipitation rate (shading) and topography (thick dotted line at 250 m and 500 m height). Vertical velocity is contoured at (a) $\pm 0.05$, $\pm 0.1$, $\pm 0.15$, $\pm 0.2$ m/s and (b) $\pm 0.5$, $\pm 2$, $\pm 10$ m/s. Precipitation rates amount up to (a) 0.2 mm/h and (b) 20 mm/h.

[6] J. B. Klemp, W. C. Skamarock, and O. Fuhrer, Mon. Wea. Rev., in press (2003).

[7] C. Schär, D. Leuenberger, O. Fuhrer, D. Lüthi, and C. Girard, Mon. Wea. Rev. **130**, 2459 (2002).

[8] C. Schär, M. Sprenger, D. Lüthi, Q. Jiang, R. B. Smith, and R. Benoit, Quart. J. Roy. Meteorol. Soc., in press (2003).

[9] C. Schär, Encyclopedia of Atmospheric Sciences. Academic Press, 1602 (2002).

[10] A. Walser and C. Schär, J. Hydrol, submitted (2003).

[11] A. Walser, D. Lüthi, and C. Schär, Monthly Weather Review, submitted (2003).

**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]Physikalisch-Meteorologisches Observatorium, Davos
[2]Institute for Climate and Atmospheric Sciences, ETH Zurich
[3]Institute for Astronomy, ETH Zurich

**Description**

The aim of the project is to evaluate the response of the global ozone and climate to the variability of the solar UV irradiance using a 3-D General Circulation and Chemistry Model. In 2002 we installed a new parameterization of the heterogeneous chemistry and updated the radiation code of the GCM to include heating rate due to absorption of UV radiation by oxygen and ozone. We have performed two 8-year long simulations for the minimum and maximum solar activity cases. The new model shows much better performance in the formation of the ozone "hole" (see Figure 33). The simulated response of the total ozone to the solar UV variability consists of a

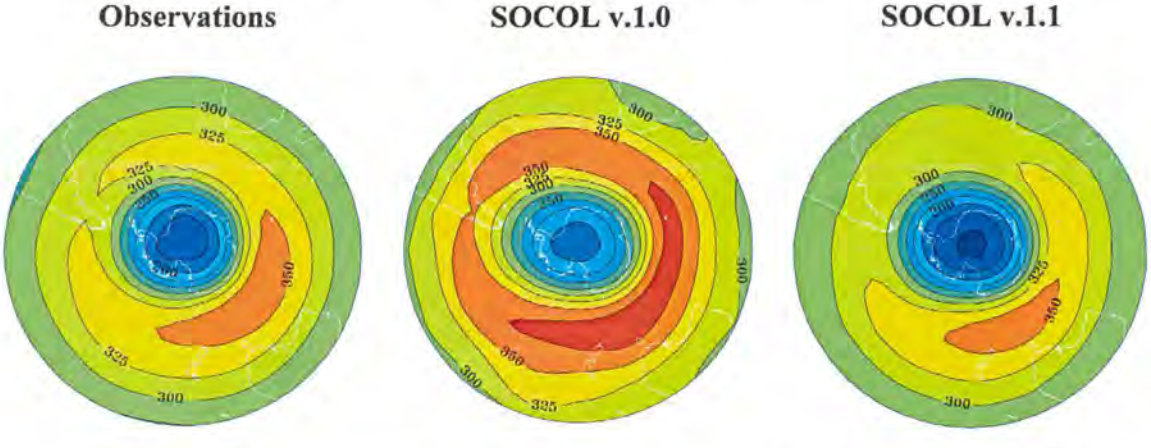



Figure 33: Observed and simulated monthly mean total ozone distribution over the southern hemisphere in October.

≈ 6 D.U. increase in the tropics and an about 8 D.U. around 30°N, which is in close agreement with the observational data. The model simulates the observed warming in the lower stratosphere well. In the middle stratosphere the model results resemble the temperature signal obtained from the satellite data (see Figure 34). The simulated solar signal in geopotential heights for February consists of the intensification of the polar vortex and development of the ridges over middle latitude area. In July the simulated geopotential height decreases slightly over the high latitude area and increases over the middle and low latitudes (see Figure 35). These results are in a good agreement with observational data.

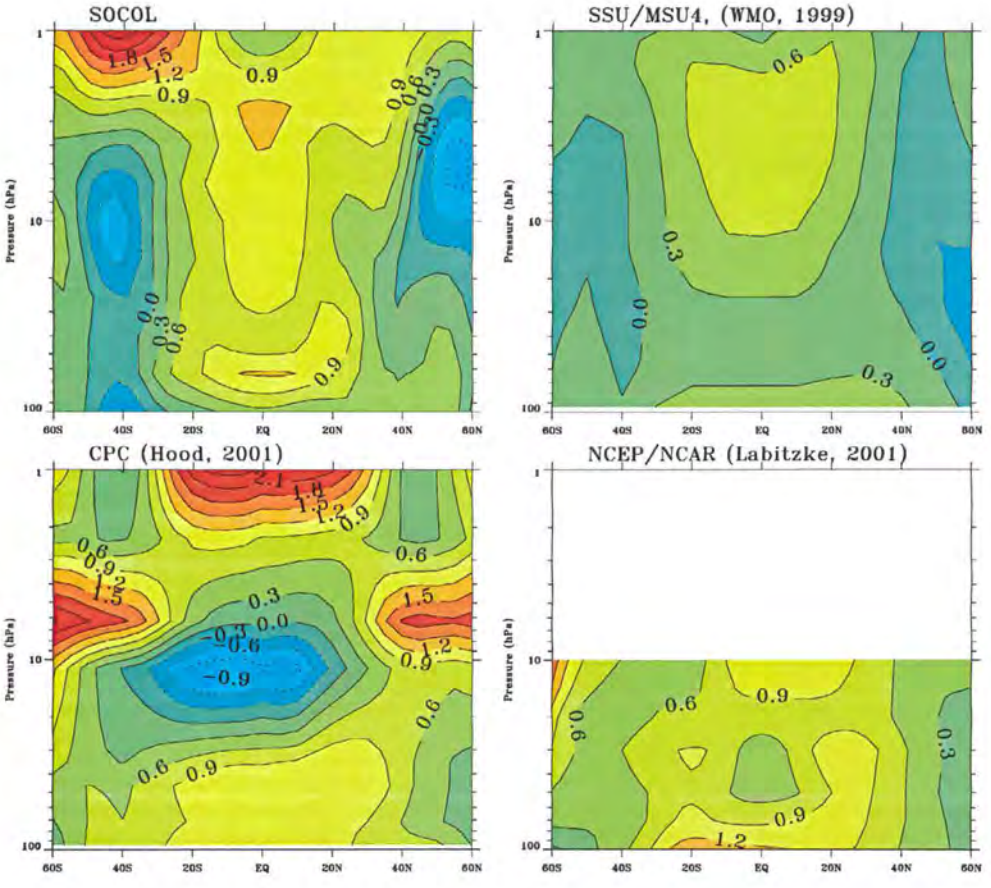



Figure 34: Latitude-height cross-section of simulated and observed solar-maximum-minus-solar-minimum changes in annually averaged zonal-mean temperature (K).

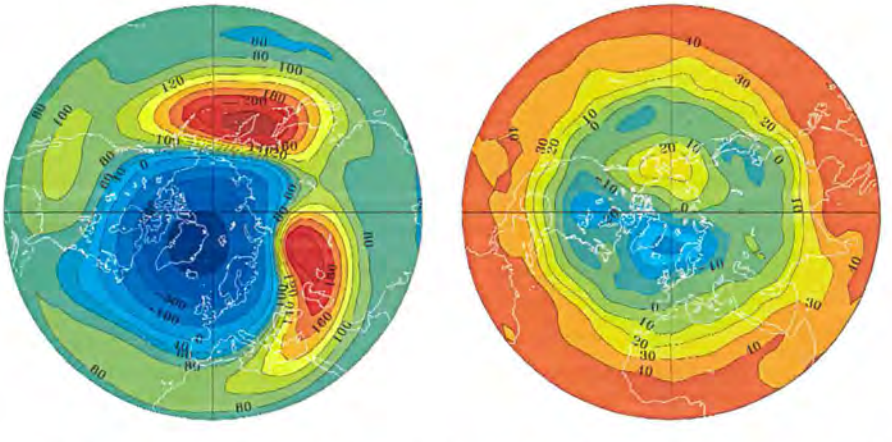


Figure 35: Geographical distribution of the simulated solar-maximum-minus-solar-minimum changes in geopotential heights (m) of 30 hPa surface for February (left) and July (right) over the northern hemisphere.

**References**

[1] E. Rozanov, T. Egorova, C. Fröhlich, M. Haberreiter, T. Peter, and W. Schmutz, ESA SP-508, p. 181 (2002).

[2] M. Haberreiter, I. Hubeny, E. Rozanov, I. Ruedi, C. Fröhlich, W. Schmutz, and T. Wenzler, ESA SP-508, p. 209 (2002).

[3] A. Nagurny, E. Rozanov, T. Egorova, and E. Medvedchenko, Meteorology and Hydrology **N1**, 35 (2002).

[4] T. Egorova, E. Rozanov, I. Karol, V. Zubov and S. Malyshev, Meteorology and Hydrology **N1**, 5 (2002).

**Project title:** MONALISA: modeling and reconstruction of north Atlantic climate system variability

**Project leader:** T. Stocker

**Researchers:** U. Beyerle
C. Raible

**Institutions:** Physics Institute, University of Bern

### Description

MONALISA (http://www.climate.unibe.ch/raible/nccr/start_p11_intro.html) is one of 13 projects in the NCCR-Climate (National Centre for Competence in Research - Climate: http://www.nccr-climate.unibe.ch). The major goal of this project is to reveal important processes and to understand underlying mechanisms generating natural climate variability. Variability on time scales of decade to century is an important area of the project. Our emphasis is placed on the variability affecting climate in the North Atlantic and European regions (see Figure 36).

In addition to a simulation of the present-day climate, we plan to obtain an ensemble of 5 to 10 simulations of the climate over the last 500 years using the NCAR (National Center of Atmospheric Research, Boulder, CO, USA) CCSM (Community Climate System Model). For the last 500 years of climate, past solar activities, volcanic eruptions, and greenhouse gas concentrations (e.g. carbon dioxide) will be taken into account.

This project requires significant amount of computations. Calculations are mainly conducted on a IBM SP4 at the CSCS. Installation of the model, and computational performance/efficiency tests have been conducted. The simulations are still in an initial testing phase. About 40 years of present-day climate has so far been obtained.

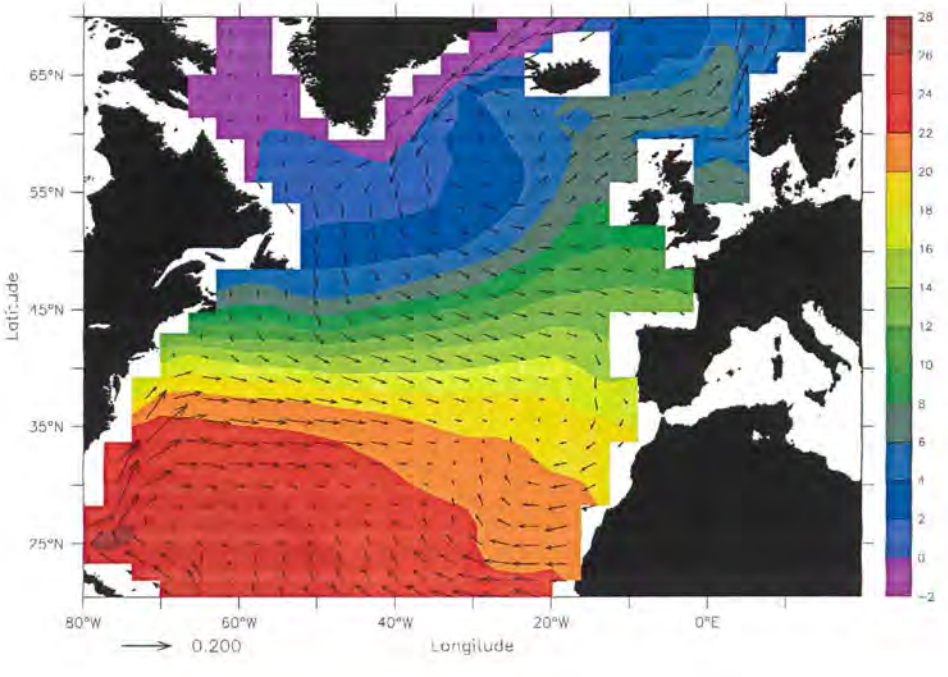



Figure 36:

**Project title:** New organic chemistry of sulfur dioxide

**Project leader:** P. Vogel[1]

**Researchers:** J. A. Sordo Gonzalo[2]

**Institutions:** [1]Laboratoire de Glycochimie et de Synthese Asymetrique, EPF Lausanne
[2]University of Oviedo, Spain

**Description**

1. Hetero-Diels-Alder and cheletropic additions of sulfur dioxide to 1,2-dimethylidenecycloalkanes. This work [1] intends to understand the factors that create the kinetic and thermodynamic competition between the hetero-Diels-Alder and the Cheletropic additions of sulfur dioxide.

2. The hetero-Diels-Alder addition of sulfur dioxide to 1-fluorobuta-1,3-dienes [2]. Unlike other 1-halodienes, 1-fluorodienes can undergo hetero-Diels-Alder addition with $SO_2$. In agreement with quantum calculations the $(E)$ isomers react more rapidly than the $(Z)$ and tend to undergo the *endo* (Alder rule) mode of cycloaddition to give fluorosultines rather than the undergoing cheletropic additions to give fluorosulfolenes. Experiments and high-level quantum calculations on the sultines confirm the existence of stabilizing enthalpic anomeric effects, which can be interpreted in terms of n(O1)$\sigma^*$(C-F) hyperconjugative interaction. This effect is strongest in the sofa conformer, which has the oxygen atom of the ring lying in the average plane of the four carbon atoms.

3. Ab initio and experimental studies on the hetero-Diels-Alder and cheletropic additions of sulfur dioxide to $(E)$-1-methoxybutadiene (see Figure 37). This work [3] demonstrates the unusual

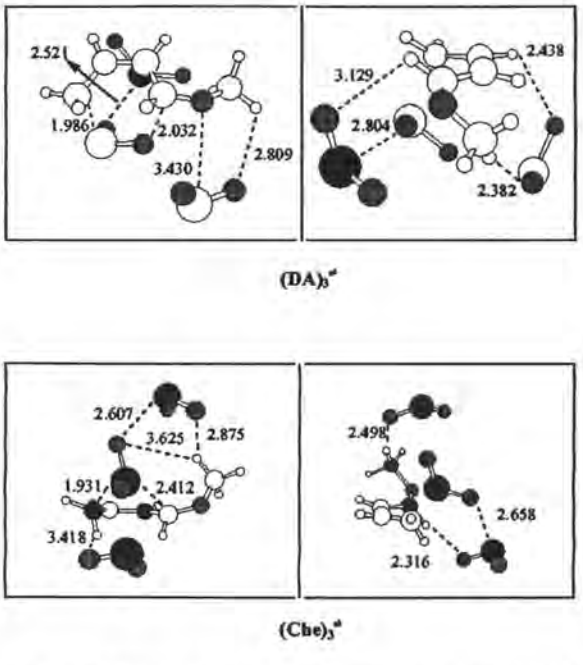



Figure 37: MP2/6-31G(d,p) and B3LYP/6-31G(d,p) transition structures with 1:3 stoichiometries located on the potential energy surfaces for the Diels-Alder $(DA)_3^{\neq}$ and cheletropic $(Che)_3^{\neq}$ reactions between $(E)$-1-methoxybutadiene and $SO_2$. All distances are given in angstroms.

properties of sulfur dioxide as reagent and solvent.

Topics under exploration:
a) Kinetic and thermodynamic deuterium isotope effects
b) Origin of the anomeric effects in sultines
c) The reactions of methanesulfonyl radical on allylic systems

**References**

[1] F. Monnat, P. Vogel, and J. A. Sordo, Helv. Chim. Acta **85**, 712 (2002).

[2] E. Roversi, R. Scoppelliti, E. Solari, R. Estoppey, P. Vogel, P. Braña, B. Menéndez, and J. A. Sordo, Chemisty Eur. J. **8** (2002).

[3] F. Monnat, P. Vogel, V. M. Rayon, and J. A. Sordo, J. Org. Chem. **67**, 1882 (2002).

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

**Project leader:** T. A. Wesolowski

**Researchers:** D. Bas
F. Tran
M. Dulak

**Institutions:** Department of Physical Chemistry, University of Geneva

### Description

The improved computer implementation of the density functional theory based orbital-free embedding formalism developed in our group [1,2] (the program deMon-KSCED [3]) was installed in Manno in October 2001. This allowed us to study larger systems in a reasonable time. The NEC implementation of the deMon-KSCED program has been used in various sub-projects [4] concerning:

- Physisorption of the hydrogen molecule on carbonaceous surfaces. The structure and the binding hydrogen molecule physisorbed on various polycyclic aromatic hydrocarbons was determined [5].
- IR spectra of probe molecules in zeolites. The microscopic origin of the CO stretching frequency shift in various zeolites has been analyzed [6]. Currently, we are investigating the interaction induced shifts of the properties of other probe molecules.
- Weakly bound complexes. The benchmark calculations testing the accuracy of the interaction energies calculated using the our method has been performed [7]. We also analyzed the geometry and the interaction energies in various complexes involving carbazole [8]. Currently we are investigating other weakly interacting complexes involving larger molecules.

### References

[1] T. A. Wesolowski and A. Warshel, J. Phys. Chem. **97**, 8050 (1993).

[2] T. A. Wesolowski and J. Weber, Chem. Phys. Lett. **248**, 71 (1996).

[3] T. A. Wesolowski, J. Chem. Phys. **106**, 8516 (1997).

[4] T. A. Wesolowski, CHIMIA **56**, 707 (2002).

[5] F. Tran, J. Weber, T. A. Wesolowski, F. Cheikh, Y. Ellinger, and F. Pauzat, J. Phys. Chem. B **106**, 8689 (2002).

[6] T. A. Wesolowski, A. Goursot, and J. Weber, in *Studies in surface science and catalysis*, edited by A. Galarneau, F. Di Renzo, F. Fujala, and J. Vedrine (Elsevier, 2001), Vol. 135; T. A. Wesolowski, A. Goursot, and J. Weber, J. Chem. Phys. **115**, 4791 (2001).

[7] T. A. Wesolowski and F. Tran, J. Chem. Phys. **118**, 2072 (2003).

[8] T. A. Wesolowski, P.-Y. Morgantini, and J. Weber, J. Chem. Phys. **116**, 6411 (2002).

**Project title:** Direct numerical simulation of condensation in air-water stratified flow

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### Description

The highly vectorized pseudo-spectral Navier-Stokes solver used as the foundation of the DNS turbulence studies was first successfully run at CSCS on the NEC SX5. The pseudo-spectral solver was first modified with the introduction of the energy equation for the gas and/or liquid phases, as a first step toward studying Direct Contact Condensation.
With the progression of this work to large problem sizes and the incorporation of heat transfer/mass transfer/condensation, the code has been ported to the IBM SP4. After initial code profiling, OpenMP parallelization of the most time-consuming parts of the code was implemented. The result of this initial effort was simulations that ran at half the speed of the same job on the NEC SX5. With more OpenMP implementation in the code, we expect the code to run at least as fast on IBM SP4 nodes as with equivalent CPU count runs on the NEC SX5.

### References

[1] M. Fulgosi, D. Lakehal, S. Banerjee, and G. Yadigaroglu, in *Proceedings of DLES-4, Direct and Large-Eddy Simulation - IV*, edited by B. J. Geurts, R. Friedrich, O. Metais (Kluwer Academic Publishers, 2001), ERCOFTAC Series Vol. 8.

[2] D. Lakehal, M. Meier, and M. Fulgosi, Int. J. Heat and Fluid Flow **23**, 242 (2002).

[3] M. Fulgosi, D. Lakehal, S. Banerjee, and V. De Angelis, Journal of Fluid Mechanics, submitted (2002).

[4] D. Lakehal, M. Fulgosi, and G. Yadigaroglu, ASME Journal of Heat Transfer, submitted (2002).

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