

6 - MODELLING

In this modelling section, we present recent development of the theoretical and numerical tools that have been developed at the LLB to predict, calculate, reduce and interpret neutron scattering spectra. The ability of neutron scattering to bring key evidences and answers to a large spectrum of scientific domains is strongly correlated with the progress made in various fields of modelling. Except pure theory that is the ultimate modelling tool, these scientific and technical efforts can be separated in three main categories:

- Provide efficient User Interfaces to fitting programs for neutron users (FULLPROF SUITE)
- Develop more realistic models and simulations (MATERIAL SCIENCE)
- Perform accurate simulations of physical systems (MOLECULAR DYNAMICS)

This chapter spans the whole spectrum of LLB research activity, from hard-condensed matter theory to material science and Molecular Dynamics simulations in life sciences. The “Magnetism and Superconductivity” chapter has described the experimental results obtained in the field of High T_C superconducting-materials. The scientific research at LLB is closely connected to the theoretical efforts performed in-house, see below and Highlight F. Onufrieva. A team from the “Centre de Biophysique Moléculaire” of Orléans had joined the LLB in order to combine, in an efficient way, Molecular Dynamics and experimental neutron scattering data in Life Sciences. Indeed, The LLB access to the new LINUX cluster farms has provided an inexpensive source of interactive, single-processor flops (floating-point operations per second), a source of batch flops during off hours and a source of multiprocessors for parallel Molecular Dynamics simulations. This new type of hardware calls for improved software methods. Take a look at the last paragraph of this introduction and at Highlight G. Kneller.

THEORY OF STRONGLY CORRELATED ELECTRONIC SYSTEMS

a) Chemical reactions and electronic transfer reactions

Electron Transfer (ET) reactions are central to many biological processes and are also of interest to the growing community interested in molecular electronics. Traditional theoretical descriptions of ET in condensed phases have focused on systems either in the high temperature limit, where nuclei can be treated classically, or in the low temperature and small electronic coupling limit, in which case nuclear modes are approximately harmonic and Fermi's Golden rule is valid. Exact, fully quantum mechanical description of complex systems in more general temperature and coupling regimes is not computationally feasible, and as a result, many studies of these regimes have utilized semiclassical approximations. Equally important is the fact that traditional rate expressions, based on the assumptions of small and constant electronic coupling or the assumption of nuclear thermal equilibrium, cannot be relied upon in the case of ultrafast ET reactions.

Understanding the role that these resonances play in chemical reactions is crucial to our basic understanding of all chemical reactivity. See Highlight S. Aubry.

b) Superconductivity

In transition-metal oxides, d-electrons experience competing forces: Coulombic repulsion tends to localize individual electrons at atomic lattice sites, while hybridization with the oxygen p-electrons tends to delocalize the electrons. These strong correlations between electrons are a central unifying factor in a wide range of phenomena, such as high temperature superconductivity, colossal magnetoresistance, the quantum Hall effect, heavy fermions and Coulomb blockade in single-electron transistors. In a large number of systems, non-Fermi liquid behaviour is replacing the Fermi liquid paradigm. The current theoretical research at the LLB focuses mainly on transitions between different ground states of a many-particle system as function of doping either with holes or with electrons. Prominent examples are phase transitions between a magnetic state at low doping and a nonmagnetic one and then a superconducting state at higher doping in the High T_C superconducting-materials. The correlation problem can be attacked with various demanding numerical and field-theoretical techniques: Exact diagonalization, Quantum Monte Carlo, Mori Zwanzig projection technique, cumulant techniques, Dynamical mean field theory and so on. See Highlight F. Onufrieva.

CRYSTALLOGRAPHY AND DATA REDUCTION IN DIFFRACTION : Recent improvements of the FULLPROF SUITE and the new FULLPROF STUDIO for visualising crystal and magnetic structures

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The **FULLPROF SUITE** is a combination of data analysis and simulation programs among which the couple **WINPLOTR** and **FULLPROF** [1-2] constitutes one of the most popular Rietveld refinement tools. These programs are used worldwide for the analysis of powder diffraction data. The treatment of incommensurate magnetic structures is one of the specialities of **FULLPROF** that other programs cannot handle [3]. During the last two years we have improved the Crystallographic FORTRAN Modules Library (**CRYSFML**) [4], which is the development framework of the full suite of programs we are distributing. Here we provide a detailed summary of the recent work done in different parts of the source code. See also Highlight M. Casas-Cabanas.

a) FullProf

During 2004, the collaboration between the LLB and ISIS, the English spallation source, concerning data analysis has been strongly developed and enhanced. Several improvements concerning the analysis of Time of Flight (TOF) powder and single crystal diffraction data have been introduced in **FULLPROF**. In particular the number of different scale factors for treating single crystal data coming from different detectors has been increased up to 24; this allows a quite easy calibration of the detector banks of instruments like SXD at ISIS using a standard single crystal sample.

In powder diffraction, we have improved the calculation of the peak shape functions that allows robust and faster refinements. The technique of simulated annealing to solve crystal and magnetic structures has also been adapted to TOF using multi-banks data. The extraction of integrated intensities, to be used in simulated annealing work, has been improved and adapted to the fact that the most important data from the point of view of structure determination are those of low Q (high TOF) appearing usually at the end of the TOF data files.

In 2004, a new kind of analysis concerning anomalous powder diffraction using synchrotron radiation has been introduced within **FULLPROF**. Thanks to the collaboration with Hervé Palancher and Jean Louis Hodeau (Laboratoire de Cristallographie, CNRS, Grenoble) we have developed new tools for exploiting the information contained in X-ray powder diffraction patterns as a function of the energy. At present **FULLPROF** is able to output calculated and observed “difference anomalous diffraction patterns” and “anomalous Fourier difference maps”. These tools are extremely important when one seeks, for instance, the cationic distribution of different chemical species in zeolites.

b) CrysFGL

The incorporation of Laurent C. Chapon from ISIS to the team working around the **FULLPROF SUITE** has boosted the development of graphics support for diffraction data analysis within suite. A new Fortran library, called **CRYSFGL**, to access OpenGL has been written (Laurent C. Chapon) implementing everything concerned with atoms and magnetic moments. The library uses the symmetry parts of **CRYSFML**, to generate all atoms/magnetic moments in a given crystal. The library implements linked list of atoms, magnetic moments and bonds allowing a dynamic loading (construction and destruction) of the different objects in complete interactivity with the user. **CRYSFGL** should be linked with one of the Fortran implementations of OpenGL existing in the market.

At present we can either use GLUT, which is completely free, or Winteracter (**WCRYSFGL**). Programs to visualise structures can be easily developed by using **CRYSFGL**. The first application we have developed is **FULLPROF STUDIO** (Laurent C. Chapon), which allows an automatic representation of the crystal and/or magnetic structure solved/refined by using **FULLPROF**.

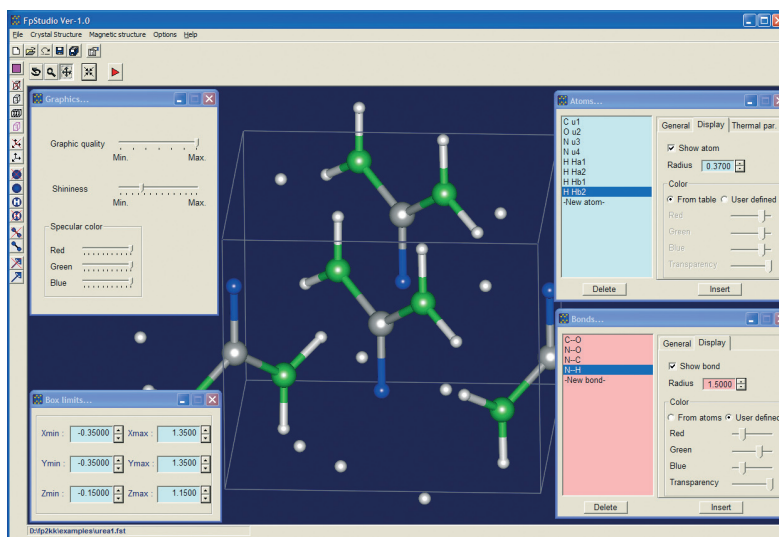


Figure 1: General view of FullProf Studio during a session on the urea structure

This application has been developed as a tool so simplify and understand what is happening in the course of a structure solution by simulated annealing or a refinement by least squares, however high quality graphics can be generated selecting the appropriate parameter in the **FULLPROF STUDIO** menu. Examples of such graphics visualisations are provided in the following figures and pages.

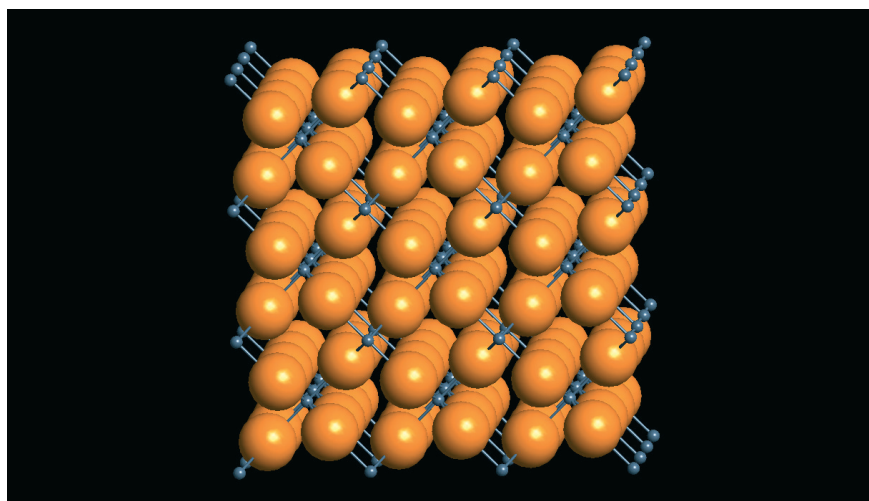


Figure 2: Oxygen packing representation of rutile TiO_2 structure

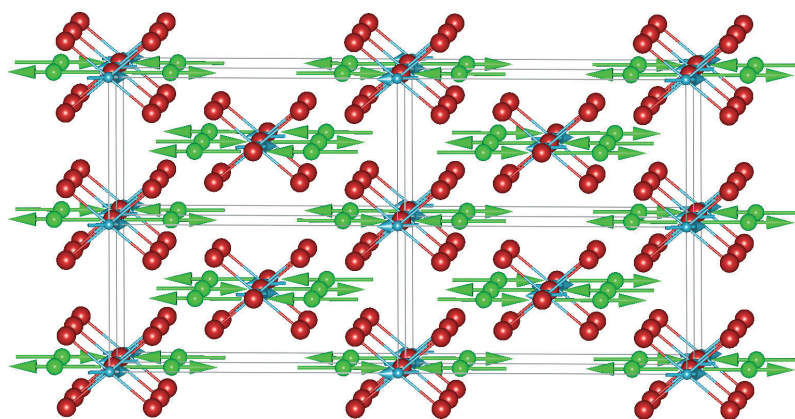


Figure 3: Magnetic structure of $\text{Ho}_2\text{BaNiO}_5$ as saved in a bitmap picture.

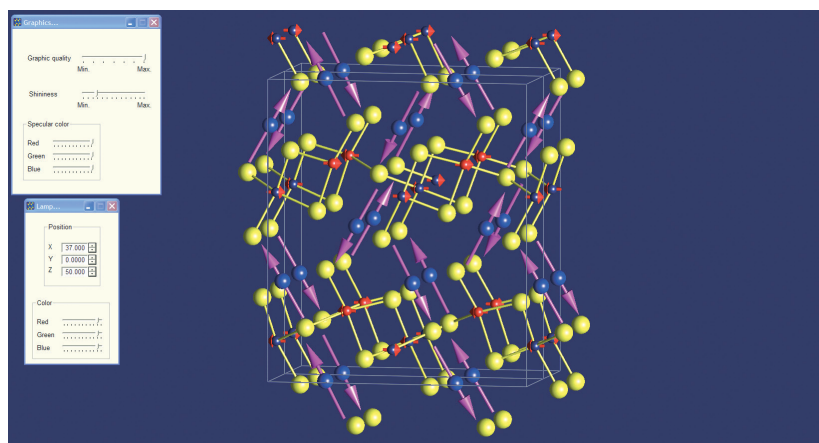


Figure 4. Changing the orientation of the illuminating lamp and graphic quality in a representation of the magnetic structure of $\text{Ho}_2\text{Cu}_2\text{O}_5$.

Other important changes have been performed within the graphical interface program, **WINPLOTR** - instrumental resolution function files, TOF, access to **FULLPROF STUDIO**, access to the new version of DICVOL 2004, Fourier filtering, etc.- and **BASIREPS**, a program for calculating basis functions of irreducible representations of space groups. See the documents within the **FULLPROF SUITE** [2] for details.

c) CrysFML

The first version of **CRYSFML** contained procedures for reading data files of many different formats, string utilities for handling the reading in free format, generation and reading of CIF files, mathematical procedures, and modules for generating space groups from their Hermann-Mauguin, user-defined generators or Hall symbols for whatever setting. Also reflection handling modules for generating reflections in selected regions of reciprocal space and for calculating structure factors were incorporated into the library. More recently we have developed a special module for calculating structure factors of incommensurate crystal structures. This is under testing and we seek the creation of a general module handling symmetry in high dimensional spaces (Aziz Daoud-Aladine).

We have also developed a module, called “Molecular_Crystals”, that is able to handle all geometrical aspects of molecules in crystals. This is the basis for the new rigid body option to be implemented in **FULLPROF** and also for the Molecular Editor (EdMol, Javier González-Platas) and Structure Determination program (StructRes, Javier González-Platas & Juan Rodríguez-Carvajal) that we are currently developing. The molecules can be described using different options, in particular the Z-matrix formalism: the free parameters are the distances, bond angles and torsion angles. This is extremely useful for the structural analysis of pharmaceutical compounds.

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The complete FULLPROF SUITE can be obtained from <ftp://ftp.cea.fr/pub/llb/divers/fullprof2k/>.
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MATERIAL SCIENCES : Monte Carlo modelling of recrystallisation processes in metals and alloys

Quantitative predictions on the microstructure and properties of metals and alloys are on the verge to be obtainable now for computer simulations of recrystallization processes [1]. Simulations can be used to predict the average texture and grain size that strongly affect mechanical behaviour [2]: refining the grain size is a low-cost way to increase both the strength and the toughness of metals. Simulations are a promising

tool to improve our understanding of the recrystallization phenomenon, a highly complex process from a microstructural point of view. The main driving force acting in these processes is the stored energy, resulting from plastic deformation, that can be evaluated from neutron scattering or Electron Back Scattering Diffraction (EBSD) techniques. The microstructural evolution inherent in recrystallization depends on the grain boundary properties, which are sensitive to their detailed crystallographic character. Computer simulation techniques that can take in account the full range of grain boundary behaviour are of great interest.

In order to simulate the recrystallization process, Monte Carlo modelling has been applied to the case of wire-drawn copper deformed to a moderate strain. Several nucleation hypotheses have been introduced and tested into the model.

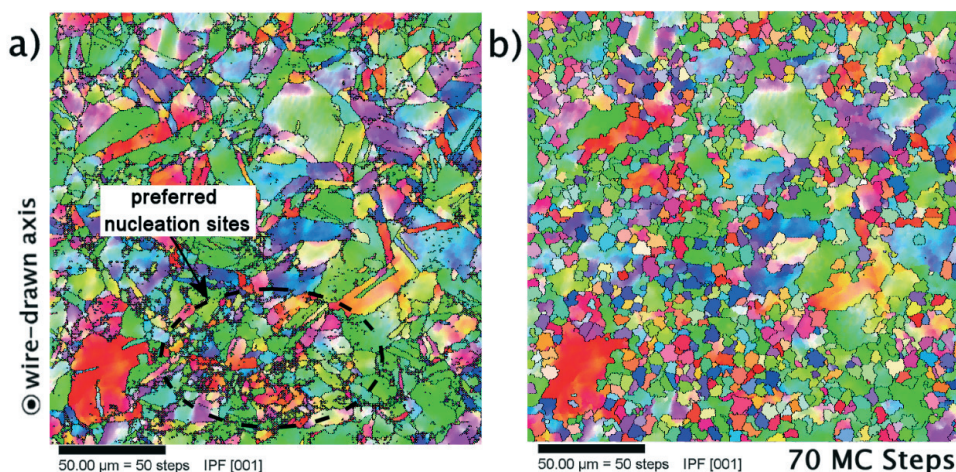


Figure. 5 a) Experimental microstructure of the deformed state measured with EBSD in wire-drawn copper.
b) Microstructure evolution after 70 MC Steps using the nucleation hypothesis connected to the sites with strong misorientation and high stored energy values.

It has been shown that nucleation taking into account the sites associated with the highest stored energy and highest local misorientation leads to the best results in terms of recrystallization microstructure and texture. An important number of new orientations - that come only from annealing twinning - are not reproduced with the model, indicating the major role of this particular mechanism during the recrystallization process. Similar studies have been also performed in cold-rolled IF-Ti steel [3].

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LIFE SCIENCES : Molecular dynamics simulations in Life Sciences

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a) Interface between Molecular Dynamics simulations and Neutron scattering

nMOLDYN is an interactive analysis tool for Molecular Dynamics trajectories, with an emphasis on quantities related to neutron scattering. The software is developed since several years and a first version has been published in 1995 [1]. nMOLDYN calculates intermediate scattering functions and dynamic structure factors, the EISF, velocity autocorrelation functions and densities of state, angular velocity autocorrelation functions, and mean square displacements. A recent addition is the analysis of molecular trajectories by autoregressive models, which permits in particular the calculation of memory functions. There are also several trajectory transformation functions and visualization aids [2].

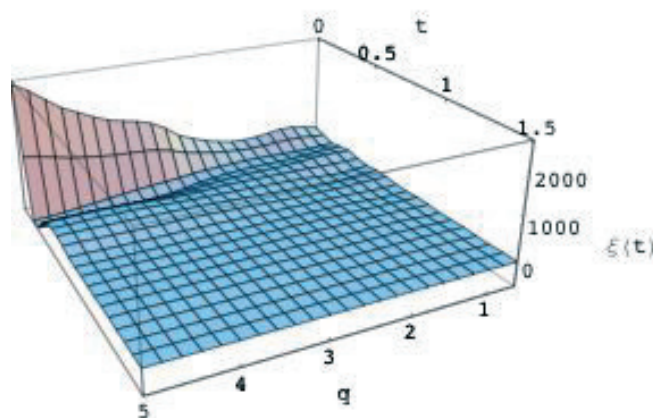


Figure 6. The memory function $\xi(q, t)$ of the coherent intermediate scattering function.

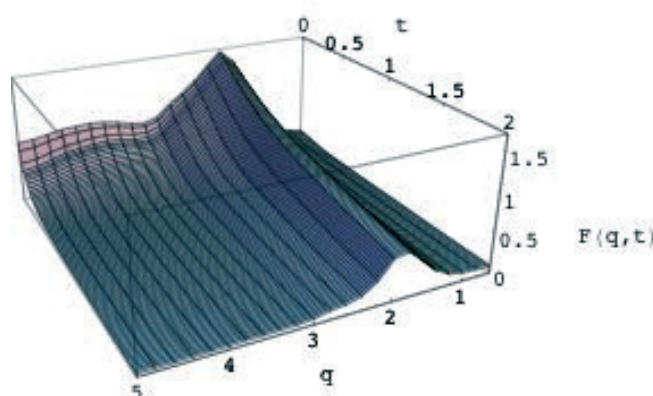


Figure 7. The coherent intermediate scattering function $S_{\text{coh}}(q, t)$.

b) Proteins dynamics: Microhydrodynamics and Fractional Brownian Motion

A characteristic feature of protein dynamics is the presence of a wide range of time scales. Correlation functions describing relaxation processes in proteins exhibit a non-exponential decay. We find that fractional Brownian dynamics is a good model for the internal dynamics of lysozyme in solution as obtained from Molecular Dynamics simulations [3]. Both the dynamic structure factor and the associated memory function fit well the corresponding analytical functions calculated from the model.

In the framework of the bilateral PROCOPE-program (2001-2003), a new collaboration was started with G. Sutmann from *Jülich* on the study of Brownian motion on the molecular level [4]. The idea is to use a new method to compute memory functions from Molecular Dynamics simulations [5] in order to perform systematic studies of the transition from deterministic Hamiltonian mechanics to Brownian dynamics and on hydrodynamic interactions on the microscopic level.

c) Protein structure prediction from electron microscopy data

Electron microscopy provides structural information about biological systems that cannot be studied by X-ray crystallography. However, the resolution of the resulting electron density maps is too low to create models at the atomic level. We have developed a computational method to predict atomic protein structures from electron microscopy data for the frequent case in which an atomic-scale structure is available for another conformation of the same protein [6]. This structure is deformed iteratively until it is compatible as far as possible with the experimental electron density map. The deformation algorithm is based on an evaluation of the local flexibility in different parts of the protein from a simple harmonic potential for a reduced protein model [7].

d) Development of molecular simulation software

In parallel to working on new computational methods for the simulation of molecular systems, we have developed a range of simulation software to make our methods (and others) accessible to the scientific community. This software is continuously maintained and extended, and is freely available for downloading.

The Molecular Modelling Toolkit [8] is a molecular simulation library that provides many standard simulation algorithms (Molecular Dynamics, energy minimization, normal modes) as well as those developed by our group. It also provides lower-level building blocks for implementing new methods, such as the definition of molecules, their manipulation, energy evaluation, and trajectory management. In addition to being used directly by simulation scripts, it can also serve as a basis for writing interactive simulation tools. Scientific Python [9] is a more general library for scientific computing. It contains all the code that is of use in more application areas than only molecular modelling. It provides standard numerical algorithms (e.g. interpolation, least-squares fits) and provides support for geometry, visualization, I/O, GUIs, and parallel computing.

e) Parallel software engineering for scientific computing

Many molecular simulations techniques require a lot of CPU time. Since parallel computers are by now nearly ubiquitous in research environments, and since many molecular simulation algorithms have been parallelized or are very easy to parallelize, one would expect parallel computing to be a standard tool in the molecular simulation community. However, parallel programming is very difficult and time consuming, which discourages most computational scientists from writing their own parallel code.

A big part of the complexity is due to the dominant parallel programming model, message passing. This model offers detailed low-level control over communication to the programmer, but also makes him responsible for all the details, in particular synchronization between processors. Moreover, the most popular message passing protocol, MPI, works only with low-level data structures; transferring complex data such as a protein structure is a very difficult task.

By combining the Bulk Synchronous Parallel model (BSP) with the high-level Python language, a parallel programming environment was produced that permits rapid development through interactive testing and debugging and lets the programmer work on a higher level of communication specification [10]. Moreover, the use of the BSP model eliminates many sources of errors in parallel programming, in particular deadlocks.

f) Development of efficient Molecular Dynamics algorithms

We have recently developed a Molecular Dynamics simulation algorithm in which intermolecular are computed by switching periodically between explicit evaluation and linear prediction from previous values [11,12]. For the moment the method been applied to a simple model liquid consisting of several hundred oxygen molecules in the liquid state. The method yields an effective speed-up of 6-7, keeping all essential structural and dynamical features of the simulated system. The work has been performed in the framework of a Marie Curie Fellowship under contract number HPMF-CT-2000-00470.

References of Molecular dynamics simulations in Life Sciences

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