Scientific Report for the Workshop within the SimBioMa programme (ESF)

«Designing and applying computational tools for reliable prediction of metal oxides properties»

Ruđer Bošković Institute, Zagreb, Croatia, May 20th -22nd 2010.

Proponents:

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Summary

This workshop was aimed for experimentalists working in the field of materials science, using methods of X ray diffraction, infrared and Raman spectroscopy, differential scanning calorimetry and others, but with insufficient knowledge of simulation techniques available today. Dr. William Smith, Daresbury Laboratory, UK, lectured on molecular dynamics simulation method with applications with DL_POLY program package. Prof. dr. Jűrgen Horbach, Institut fűr Materialphysik im Weltraum, Kőln, Germany, gave several talks on Monte Carlo method and in particular on semigrand-canonical ensemble for description of binary mixtures. Dr. Mathieu Fèvre, ONERA, France, focused in particular on yttria doped zirconia, showing a way to model realistic configurations by Monte Carlo – using neutron scattering form factors for comparison, and how to calculate thermal conductivity by moleular dynamics method. Calculating electronic structures for this type of systems is not straight forward, and prediction of carrier mobility is in particular a demanding task. We therefore invited dr. David Muñoz Ramo from London Centre for Nanotechnology to come and lecture on the prediction of self-trapping of polarons in metal oxides, since there is possibility this mechanism might appear also in ZrO_2 and similar systems. It was pointed out that Car-Parrinello 2000 program is freely available online and contains soft pseudopotentials that could be used for prediction of polarons. Prof. Ivo Batistić from Faculty of Science, Zagreb, discussed polarons in graphene nanoribbons and dr. Jelena Macan from Faculty of Chemical Science and Engineering gave a talk on transition metal oxides synthesis and properties. Dr Igor Lukačević calculated soft phonons in BaO using ABINIT program, presenting us both with an overview of density functional method as applied to phonon calculation, as with hands-on example we repeated individually. All participants had a laptop computer borrowed from R. Bošković Institute's library at their disposal for all three hands-on sessions, and Mr. Željko Litvić was of great help during those exercises.

All lectures were greatly appreciated by the audience, and agreement was made that any further assistance if needed would be passed on using e-mail.

Workshop report

There is a growing community of scientists engaged in computational physics in Croatia. The aim of the workshop was to bring molecular dynamics and Monte Carlo methods closer to experimentalists who are working in the field of materials science, demonstrating the state-of-the-art methods, but at the hands-on level. As a particular topic we proposed transition metal oxides whose significance lies in extended use in engineering applications. TiO_2 in anatase form is known as photocatalytically active material, used for solar energy conversion, while the rutile phase is used as a white pigment. ZrO_2 has high toughness, low thermal but fast ion conductivity on doping with Y_2O_3. There is a longstanding interest in these materials at Ruđer Bošković Institute, Zagreb, Croatia, where new synthesis routes are being designed for these ceramics, and scanning electron microscopy, X-ray diffraction and Raman spectroscopy are routinely used for their characterization[1-4]. On the other hand, e.g. Monte Carlo technique is used but not widely spread[5].

Hoping to bring these computational tools closer to our community, we proposed as lecturers - dr. William Smith from Daresbury Laboratory, UK, prof. Jűrgen Horbach, Institut fűr Materialphysik im Weltraum, Kőln, Germany, dr. Mathieu Fèvre from ONERA (The French Aerospace Lab), and dr. David Muñoz Ramo from London Centre for Nanotechnology, UK.

Dr. W. Smith is the author of the DL_POLY molecular dynamics package[6], and has studied atom-atom potentials suitable for molecular dynamics calculation of TiO_2 sequence of structures and its properties[7], while dr. Fèvre studied thermal conductivity in yttria-doped zirconia using molecular dynamics starting from configurations prepared with Monte Carlo method and checked against diffuse neutron scattering maps[8,9]. As Monte Carlo method is absolutely indispensable tool for these systems, prof. Horbach agreed to lecture us both on basics of the method as well as on its application to transition metals in particular[10]. Dr. Muñoz Ramo recently theoretically predicted self-trapping of electrons and holes in HfO_2 [11]. Since electron polaron is predicted for TiO_2 [12], it is likely one or both types could be present in ZrO_2 and $ZrTiO_4$ as well, fact which is important for determination of the conductance behaviour in these compounds.

This workshop was also an opportunity for people outside Croatia capital, Zagreb, to come and participate both by learning about computational programs as by meeting the scientists rom Ruđer Bošković Institute, Institute of Physics, Faculty of Science and Faculty of Chemical Science and Engineering who are leading most of the research on transition metal oxides in Croatia.

On the first day dr. William Smith introduced the topic of molecular dynamics simulation and gave an overview of DL_POLY program package. Assembling and creating configurations, suitable potentials and results analysis was demonstrated in many examples. All participants had at their disposal laptop computers (notebooks) provided by ruđer Bošković Institute's library (Fig. 1. and Fig. 2).

Fig1.

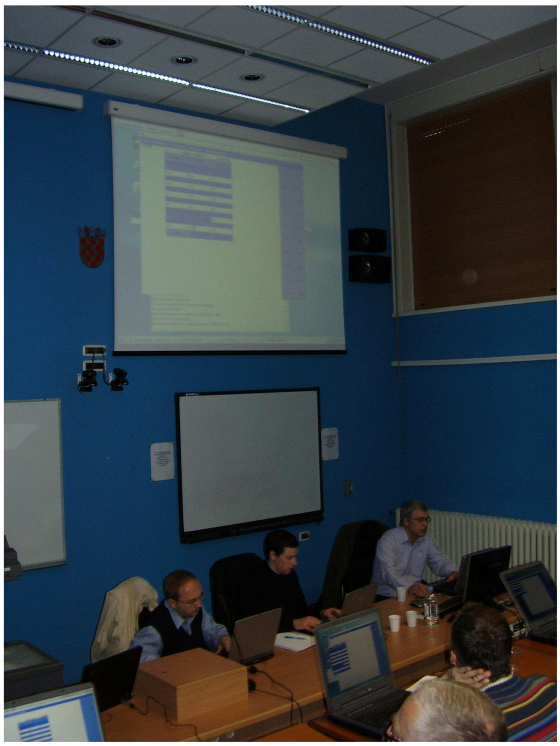

Fig. 2.

Prof. Jűrgen Horbach gave several lectures on Monte Carlo method explaining importance sampling, detailed balance, Metropolis algorithm and its implementation. In particular and responding to our interest, he described semigrand-canonical Monte Carlo ensemble. As a practical example, a program calculating probability distributions of a mixture of two phases interacting with Lennard Jones potential around T_c was run by each participant as an exercise. Implementation of the method to the mixture of two metal oxide compounds AO_2 and BO_2 wa discussed.

Dr. Mathieu Fèvre from ONERA gave a detailed talk describing modelling of thermal conductivity in zirconia based systems. Subsequent zirconia/yttria structures were generated by acceptance or rejection of possible structures whose form factors were compared with experimental neutron scattering results. Thermal conductivity was calculated with nonequilibrium molecular dynamics. Prof. Ivo Batistić gave a talk on polarons in graphene nanoribbons, while dr. David Muñoz Ramo presented his results on stable electron and hole polarons in HfO_2 and more generally explained how to investigate polaron states using density functional methods. It was suggested that academically freely available CP2K (Car-Parrinello 2000) program has all the features necessary for calculation of possible polaron states in strongly interacting organic crystals.

Dr. Igor Lukačević dedicated his lecture to soft modes in semiconductors calculated by ABINIT , and presented his results for BaO calculated specially for this workshop. The case of ZrO_2 polymorphism and new advances in the literature regarding the prediction of its polymorphism were the subject of discussion. Dr. Jelena Macan as an experimental chemist gave a talk on synthesis and properties of $ZrTiO_4$ and similar compounds.

Most listeners came from laboratories within Ruđer Bošković Institute, some were from Split and some from Osijek, and most listeners were new to computer simulations. Since the time for questions was limited, it was suggested that all further help would be provided via e-mail correspondence, individually to each interested participant.

List of invited lecturers:

Dr. William Smith, Daresbury Laboratories, UK
Prof. Jűrgen Horbach, Institut fűr Materialphysik im Weltraum, Kőln, Germany
Dr. Mathieu Fèvre, Office National d'Etudes et de Recherches Aéronautiques, France
Dr. D. Muñoz Ramo , London Centre for Nanotechnology, UK
Dr. Igor Lukačević, University J. J. Strossmayer Osijek, Croatia
Prof. Ivo Batistić, Faculty of Science, Zagreb, Croatia
Dr Jelena Macan, Faculty of Chemical Engineering and Technology Zagreb
Dr. Maja Buljan, Ruđer Bošković Institute, Zagreb

List of participants:

Dr. Jasminka Popović, Ruđer Bošković Institute
Dipl. ing Mirjana Bijelić, Faculty of Science, Zagreb
Dr. Biserka Gržeta, Ruđer Bošković Institute
Dr. Iva Movre-Šapić, Faculty of Chemical Engineering and Technology, Zagreb
Dr. Vesna Volovšek, Faculty of Chemical Engineering and Technology, Zagreb
Dr. Eduard Tutiš, Institute of Physics, Zagreb
Dr. Andreja Gajović, Ruđer Bošković Institute
Dipl.ing. Milivoj Plodinec, Ruđer Bošković Institute
Dr. Goran Štefanić, Ruđer Bošković Institute
Dr. Franjo Sokolić, Faculty of Science, Split,
Dipl.ing Bernarda Kežić, Faculty of Science, Split
Prof. Ivana Ivković, University of JJ Strossmayer, Osijek
Vedran Đerek, student
Dr.Marko Karlušić, Ruđer Bošković Institute
Dipl. ing. Martina Vrankić, Ruđer Bošković Institute
Dr Berislav Perić, Ruđer Bošković Institute
Dr Vjeran Gomzi, Faculty of Pharmacy, Zagreb
Dr Goran Kovačević, Ruđer Bošković Institute
Dipl. ing Fabijan Pavošević, Ruđer Bošković Institute

References:

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2. J. Macan, H. Ivanković, A. Gajović: Porous zirconium titanate ceramics synthesized by sol–gel process, *J. Eur. Ceram. Soc.* **29** (2009) 691-697.
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6. http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/index.shtml
7. D. R. Collins, W. Smith, Daresbury Laboratories Technical Report DL-TR-96-001.
8.. Fèvre, A. Finel, R. Caudron: Local order and thermal conductivity in yttria-stabilized zirconia. I. Microstructural investigations using neutron diffuse scattering and atomic-scale simulations *Phys. Rev.* **B 72** (2005) 104117.
9. M. Fèvre, A. Finel, R. Caudron, R. Mévrel, Local order and thermal conductivity in yttria-stabilized zirconia. II. Numerical and experimental investigations of thermal conductivity *Phys. Rev.* **B 72** (2005)104118.
10. http://www.cond-mat.physik.uni-mainz.de/~horbach/publications.html
11 D. Muñoz Ramo, A. L. Schluger, J. L. Gavartin, G. Bersuker,: Theoretical Prediction of Intrinsic Self-Trapping of Electrons and Holes in Monoclinic HfO_2, *Phys. Rev. Lett.* **99** (2007) 155504.
12 N. A. Deskins, M. Dupuis: Electron transport via polaron hopping in bulk TiO_2: A density functional theory characterization, *Phys. Rev.* **B75** (2007) 195212.

Results of the workshop: dissemination of knowledge

Most listeners came from laboratories within Ruđer Bošković Institute, some were from Split and some from Osijek, and most listeners were new to computer simulations. Several participants had a background in quantum chemical calculations (Gaussian03), some were experienced crystallographers and spectroscopists. At the beginnig an introductory welcome talk was given, urging scientists to apply for short visit or exchange grants within SimBioMa programs (PESC in particular) and describing how one could actively get involved in the ESF.

Greatest interest was aroused when the subject of polymorphism was raised. While Dr. Smith presented Rahman-Parrinello molecular dynamics method for simulation of phase transitions, dr. Fèvre gave a phase diagram of Y_2O_3 doped ZrO_2 and a figure depicting corresponding temperature dependent cation diffusion. The polymorphsim of ZrO_2 was discussed in view of phonon-phonon interaction which could lead to stabilization of cubic phase at room temperature.

Since the time for questions was limited, it was suggested that all further help would be provided via e-mail correspondence, individually to each interested participant.

Final workshop programme:

time	20. V 2010. Thursday	21. V 2010. Friday		22. V 2010. Saturday	
9:00-9:45	dr. W. Smith Introduction to molecular dynamics simulation	9:30-10:30	dr. W. Smith hands-on DL_POLY	9:00-9:45	dr. I. Lukačević: Soft modes in BaO calculated by ABINIT
9:45-10:30	dr. W. Smith DL_POLY 1			9:45-10:30	hands-on ABINIT
10:30-11:00	coffee break	10:30-11:00	coffee break	10:30-11:00	coffee break
11:00-11:45	prof. Jűrgen Horbach Introduction to Monte Carlo method I	11:00-11:30	dr. M. Buljan: Application of Monte Carlo	11:00-11:45	dr. Jelena Macan Synthesis and properties of transition metal oxides
11:45-12:30	dr. M. Fèvre: Modeling of the thermal conductivity in zirconia based systems at the atomic scale	11:30 – 12:30	prof. Jűrgen Horbach Semigrand-canonical MC	11.45-12:30	discussion
12:30-14:00	lunch	12:30-14:00	lunch		THE END
14:00-15:30	dr. W. Smith DL_POLY 2	14:00-15:30	dr. D. Muñoz Ramo: Investigation of polaron states using ab initio methods		
15:30-16:00	coffee break	15:30-16:00	coffee break		
16:00-17:00	prof. I.Batistić Polarons in graphene nanoribbons	16:00-17:00	prof. Jűrgen Horbach Hands-on Monte Carlo		