ESF-Science Meeting-Final Report

Reference Number: 2837

Title: Advances in the Implementation of Polarizable Force Fields for Molecular Simulations

Location : CECAM-EPFL, Lausanne, Switzerland
Dates: Jun 07, 2010 - Jun 09, 2010

Co-organizers :

Elvira Guardia
Universitat Politècnica de Catalunya, Barcelona, Spain

Marco Masia
Dipartimento di Chimica - Universita' di Sassari, Sassari, Italy

1) Summary

The idea of organizing a workshop came out from our perception that the use of polarizable force fields is still limited to a small niche of researchers, and that its spread to a wider simulation community is somehow damped by myriad applications of nonpolarizable force fields in modeling complex systems. In this atmosphere, it was decided to gather the researchers to focus on current research on polarizability and polarizable force fields and to boost its applications, from molecular biology to medicinal chemistry and materials science.

The workshop was meant to provide an opportunity for computational scientists from different branches of science to discuss the state of the art in the field of polarizable force fields (applications and methodology). We invited experts active in the field, both with theoretical and applied contributions, but we also aimed (and obtained) at having a vibrant participation of junior researchers and of newcomers to the field. We reached the maximum number of participants allowed (50) and we had to make a waiting list. More than 30 people had not been admitted because of the limited number of seats. To understand the interest in this topic it suffice to say that the participants' home affiliations covered 13 countries.

2) Description of the scientific content of and discussion of the event

There have been 25 presentations between invited (14) and contributed (11) speakers. The topics faced by all of them can be gathered into three main categories:

1- Applications:

Simulation results on heterogeneous systems have been presented; in particular the most important fields of application are biophysics, ionic liquids, ions in bulk water or at air/water interface, and molten salts. For homogeneous systems, results have been shown for a polarizable force field giving highly accurate description of dynamical and statical properties of pure water.

2- Methods to Parameterize Force Fields:

We can devise three approaches based on the fit of reference data. The reference data could be obtained by (i) high level Quantum Chemical calculations of small clusters at gas phase, (ii) first principles molecular dynamics calculations, and (iii) experimental measures. Most of the people involved in force field parameterization use mainly the first and the second approach; in particular the second approach is the one which is growing fast with new methods as the force matching algorithm (applied to water and molten salts) and the orbital localization method (molten salts).

3- Implementation Methods:

Technical details about implementation regard the way of including polarizability in the model and the way of accelerating the calculations. The most widespread models can be gathered in three categories: (i) the Drude model (or small variation of this model as Shell and Charge on Spring models), the Polarizable Point Dipoles method (PPD) and, (iii) the charge equalization method. The first one seem to be the most widely used by the participants at the conference. The second one is as well quite spread, mainly in implementations which require damping of electrostatic interactions; the use of such method has been shown in one presentation. Finally we should mention the use of the Always Stable Predictor Corrector (ASPC) method to accelerate the convergence of dipoles calculation in the PPD method, and the use of "coloured" Langevin thermostats to accelerate the equilibration of a system. The two methods can be used also in ab initio molecular dynamics calculations.

We organized the sessions to give the possibility of discussing the points raised in each presentation; most of sessions have fostered interesting discussions about the main points shortly explained in the previous section. In general all the lectures and review talks were at very pedagogical level, the research talks clear and compact; the discussion they raised was lively,

especially during the breaks, and several new contacts were made. We found that the mixture of people having a bit different backgrounds but still interested in a certain topic is a fruitful ground for new ideas.

On the last day we opened a round table to discuss open issues and the future of the field. Most of the participants agree that in the immediate future polarizable force fields will be implemented in most general purpose Molecular Dynamics codes and that their use will prevail on simple point charge methods. The main concern for polarizable force fields is about their quality. Methods to address this problem have been proposed in the workshop.

During the discussion, it has become clear that many paths are now open for next generation force fields: one goes in the direction of improving the description of electrostatic interactions by including higher order multipolar interactions. The other, somehow parallel to this, is to include polarization in the molecular mechanics part of QM/MM simulations; in this case the system of interest would be described by refined ab initio techniques and the environment and its dynamical response to changes in the QM part would be faithfully reproduced by the MM part.

The main limitation of the polarizable force field in use is that they do not account for intermolecular charge transfer, which could be relevant in heterogeneous systems with high electric fields. One possible evolution of polarizable force fields would be in the description of charge transfer phenomena, but no ideas have come up to propose a way of doing it.

Finally, it has been pointed out that coarse grained force fields still lack of accuracy; it has been proposed that they would benefit polarizable interactions would be included in their schemes.

3) Assessment of the results and impact of the event on the future direction of the field

At the moment of organizing the meeting we expected that a relatively small amount of people would be interested in it. Moreover, considered the huge number of CECAM workshop which had been organized this year, we were afraid of not being able to reach a reasonable number of participants. On the contrary, the outcome of the workshop was much better than what expected. Expert scientists from all the world gathered and discussed about state-of-the-art methods and applications. All the sessions were organized in such a way that long discussions (10 to 15 minutes) could take place. We were surprised to see that, for all sessions, thourough discussions took place and that most of them continued after the formal sessions. The discussions fostered the establishment of new collaborations among some participants. Most importantly they have allowed to pave the way of future developments both in the theoretical and applied approaches. Most of people agreed that the implementation of polarization in molecular simulations is the way to improve our insights of the physico-chemical properties of many systems, from interfaces to proteins and materials.

Due to the limited number of admitted participants the only weak point of the workshop is that few PhD students could participate. Though, to extend the reach of the workshop to people who could not attend it, all presentations have been uploaded on the workshop pages at CECAM and are accessible to anybody for download.

Considered the high success of the meeting we think that future meetings on the topic should be organized. Although the importance and the impact of polarizable force fields in the description of important systems, we feel that still a small community makes use of them. For the future we envisage three ways to broadening the field to more people and more applications. The first is to organize tutorials and schools for young researchers (MSc and PhD students). Then, general purpose codes should be written to handle polarization with the most common techniques (to our knowledge only few of such codes could deal with some of techniques). Finally, meetings and symposia with ca. 100 participants should be organized to address both theoretical and applied issues. The above objectives could be easily reached in a collaborative environment between people devoted to the research in the field. The meeting funded by ESF and CECAM could represent the first step in this direction. We auspicate that these and/or other institutions will fund further initiatives in this direction.

4) Final programme of the meeting

Day 1- June 7, 2010

Session I- Opening and Invited Lectures
Chair: Paul Popelier

- 9:00 to 9:15 – Welcome
- 9:15 to 10:00 – **Sotiris Xantheas**, *Ab initio based transferable interaction potential for water: simulations of water clusters, liquid water, ice and hydrate networks*
- 10:00 to 10:45 – **Daniel Spångberg**, *Shell-model polarizable force-fields for solvents and solvated ions from ab initio simulations*

10:45 to 11:15 – Coffee Break

Session II- Invited Lectures
Chair: Alexander MacKerell

- 11:15 to 12:00 – **Mathieu Salanne**, *Computing condensed-phase polarizabilities of indicidual molecules and ions*
- 12:00 to 12:45 – **Pavel Jungwirth**, *Effects of polarization on the behavior of ions and water*

12:45 to 14:30 – Lunch

Session III- Invited Lectures
Chair: Francesco Paesani

- 14:30 to 15:15 – **Collin Wick**, *The importance of polarizability and its implementation for understanding aqueous interfacial and bulk ion solvation*
- 15:15 to 16:00 – **Jiri Kolafa**, *Molecular dynamics of polarizable models*

16:00 to 16:30 – Coffee Break

Session IV- Contributed Talks
Chair: Marco Masia

- 16:30 to 16:55 – **Luigi Delle Site**, *Scales' interplay for the electrostatic properties of molecular liquids: local v. s. global*
- 16:55 to 17:20 – **Othmar Steinhauser**, *Many-body polarization forces in room temperature molecular ionic liquids (RTMIL): simulation and dielectric theory*
- 17:20 to 17:45 – **Sandeep Patel**, *Applications of charge equilibration force fields to biological systems*
- 17:45 to 18:10 – **Ivo Nezbeda**, *The multi-particle sampling method in*

Monte Carlo simulations on fluids and its efficient implementations

Day 2- June 8, 2010

Session V- Invited Lectures
Chair: Sotiris Xantheas

- 9:00 to 9:45 – **Roland Netz**, *Ions at interfaces: polarizable versus non-polarizable force fields*
- 9:45 to 10:30 – **Alexander MacKerell**, *Development of a polarizable empirical force field based on the classical Drude oscillator*

10:30 to 11:00 – Coffee Break

Session VI- Invited Lectures
Chair: Pavel Jungwirth

- 11:00 to 11:45 – **Anna-Pitschna Kunz**, *On accounting for polarizability in biomolecular simulations*
- 11:45 to 12:30 – **Rodolphe Vuilleumier**, *Use of maximally localized Wannier orbitals to build classical force fields from ab initio simulations*

12:30 to 14:30 – Lunch

Session VII- Invited Lectures
Chair: Rodolphe Vuilleumier

- 14:30 to 15:15 – **Francesco Paesani**, *Infrared spectroscopy of aqueous systems from quantum simulations with the polarizable TTM3-F model*
- 15:15 to 16:00 – **Paul Popelier**, *Quantum chemical topology: multipole moments and machine learning*

16:00 to 16:30 – Coffee Break

Session VIII- Contributed Talks
Chair: Collin Wick

- 16:30 to 16:55 – **Jonàs Sala**, *Polarizable water force field from force and dipole matching of Carr-Parrinello data*
- 16:55 to 17:20 – **Javier Hernández-Rojas**, *New models for the polarization of carbonaceous seeds*
- 17:20 to 17:45 – **Toon Verstraelen**, *The electronegativity equalization method and the split charge equilibration applied to organic systems: parameterization, validation and comparison*
- 17:45 to 18:10 – **Giovanni Bussi**, *The Langevin equation with colored noise for constant-temperature molecular dynamics simulations with polarizable force fields*

19:30 to 22:00 – Dinner

Day 3- June 9, 2010

Session IX- Invited Lectures
Chair: Daniel Spångberg

- 9:00 to 9:45 – **José L. F. Abascal**, *On the path to an accurate force field for water: lessons from simple models*
- 9:45 to 10:30 – **Riccardo Spezia**, *Developing a polarizable potential for solvation of a whole classical series: the case of Lanthanoids (III) hydration*

10:30 to 11:00 – Coffee Break

Session X- - Contributed Talks and Closure
Chair: Anna-Pitschna Kunz

- 11:00 to 11:25 – **Pår Söderhjelm**, *Transferability of QM-derived polarizable potentials*
- 11:25 to 11:50 – **Claude Millot**, *Quantum chemical calibration of distributed polarizability models for the molecular simulation of imidazodium-based room temperature ionic liquids*
- 11:50 to 12:15 – **Ivan Gladich**, *Heavy halide air-water surface affinity in aqueous solutions of mixtures of sodium salts*

12:15 to 12:50 – Discussion
12:50 to 13:00 – Closing word