Final Report

Workshop "Electrostatic Effects in Soft Matter: Bringing Experiments, Theory and Simulation Together"

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) and
MatGas Research Center

Campus de la UAB, Bellaterra, Spain
April 10th-11th, 2008

Organizing Committee

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Web Site

http://www.icmab.es/softmatter2008/

Financial Support

European Science Foundation (SimBioMa programme)
Consejo Superior de Investigaciones Científicas CSIC (Spanish National Research Council)

1.Summary

Soft matter is an emergent paradigm describing systems such as polymers, colloids, surfactants, membranes, biomaterials and their composites from a broad and interdisciplinary perspective connecting statistical physics, physical chemistry, material science and biology. The relevant processes and phenomena in these systems are characterized by length and time scales spanning from microscopic to mesoscopic scales in the same sample and experiment. Despite its importance, the foundations of the subject remain highly controversial as evidenced in recent review articles. Many simulation and theoretical models are still too far from the complexity of real experimental situations and it is not clear to what extend they capture the essential physical or chemical mechanisms. Experimental results show great complexity and strong system specificity, difficult to incorporate into simple simulation models or theories. It is also difficult to directly test basic theoretical hypothesis or even experimentally deduce possible mechanisms to be tested by simulation.

This was the motivation for the workshop, focused on solving the urgent need of bringing together experimentalists and developers of new simulation techniques and theoretical approaches, providing a forum for research discussions and foster future collaborations to significantly advance the field in a trully interdisciplinary way.

The format of the workshop allowed participation of scientists of very different backgrounds, expertises, ages and promoted an easy interaction between them.

Overall, we had 4 keynote talks (45 minutes), 8 invited lectures (30 minutes), 9 oral contributions (20 minutes), 15 posters and a round table/discussion session (2 hours) focusing on the hot topics identified during the workshop. We included not only simulation talks but also experimental talks in all relevant topics in order to facilitate a trully interdisciplinary discussion. In this line, we also included a few overview talks from groups performing both experiments and simulations in some specially relevant systems (biocolloids, DNA,..). The level of discussion and participation during the round table was intense, specially between scientists with different backgrounds (Physics, Chemistry, Materials Science) and different approaches (simulations, experiments).

We had about 60 participants from 7 UE countries, USA, Australia, Israel and Singapore. Some of the participants were postdoctoral fellows and PhD students of senior participants. Registration to the workshop was free (no fee) and many expenses were included (workshop materials, coffee break, refreshments and lunches were free to all participants, other expenses such as transportation and accommodation were refunded for invited/keynote speakers and students). The fact that the workshop was inexpensive was especially attractive for young researchers and made possible their participation and interaction with well known experts.

2. Description of the scientific content of and discussion at the event

A truly interdisciplinary discussion was successfully accomplished by designing the workshop with the following distinguishing features:

- We invited a number of well-known speakers to give more broad "overview" talks, providing a unified background for subsequent talks and discussion.

- In each session, the series of simulation talks were preceded (or followed) by an experimental overview talk, in order to facilitate comparison between experiments and simulation. Also, talks directly comparing experiments and simulations were included.

- We organized a round table/discussion session (nearly 2 hours of discussion) focusing on the hot topics identified during the workshop.

A variety of softmatter systems and methodologies were discussed during the workshop. The debate developed around four main topics:

1) ***Charge inversion and failure of classical electrostatic theories of softmatter*.**

   In general, the failure of classical theory of solution electrostatics is observed near many different softmatter interfaces (membranes, colloids, DNA,...) in the presence of multivalent ions. The problem of charge inversion (a charged interface attracting ions of opposite charge in excess of its own nominal charge) is a clear manifestation of this failure. The keynote talk of Prof. Lyklema reviewed the basic experimental facts and pointed out to the different and sometimes inconsistent or "had hoc" explanations proposed for the different observations. It was clear that currently, there is no predictive theory capable of predicting the charge inversion phenomenon although several theories seem to partially explain particular systems under specific conditions. The keynote talk of Prof. Roland Kjellander showed the theoretical basis for the failure of classical theory and developed the main ideas arising from numerical solutions and simulations of simple "toy models" in which charge inversion is observed. The invited talks of Dr. Travesset and Prof. Mas showed direct comparison between experimental results and all atomic simulations (nanofluidic devices with divalent electrolyte solution in the first case and large polyelectrolytes in divalent electrolyte solution in the second case). The results were interpreted as an evidence for electrostatic pairing between discrete interfacial charges and the divalent electrolyte, an interpretation which was controversial. The actual relevance of this "interfacial pairing" observed in simulations and other alternative possible explanations of experimental data were discussed in detail during the break and in the final round table. The contribution by Dr Martin-Molina analyzed by MonteCarlo simulations the validity of several very popular OCP models proposed to generalize classical Poisson-Boltzmann theory in the case of multivalent ions. Simulation results showed clearly the limitations of these models and

the problems arising by interpreting experimental data in terms of these models.

2) Particle stability and Colloidal interactions beyond DLVO theory.

The keynote talk by Prof. Roque Hidalgo showed an extensive comparison between electrophoretic measurements of latex colloids in different divalent and trivalent electrolyte concentration and simulations and integral equation theories. The results showed clear limitations of the most up to date simulation and theoretical techniques, which were able to reproduce only qualitatively the observed experimental trends. The invited talk by Dr Esquena showed the experimental results for the interactions between a new class of functionalized colloids. The contributed talks by Dr Duque and Dr Trulsson showed computer simulations of functionalized nanoparticles and colloids and latexes in dendrimer solutions, respectively. The simulation results are promising in the sense of predicting trends and molecular mechanisms but still fail to quantitatively predict the observed experimental features. The complex relation between charge distribution in a colloid and its electrophoretical behavior was discussed by the invited talk by Dr Pagonabarraga, showing the promising results of different mesoscopic simulation techniques. Overall, the need for more detailed models in the simulations and the need of include the details of charge distribution in colloids and explicit water was clear during the discussion.

3) Electrostatics of biological softmatter (membranes, DNA,...).

Several talks showed the importance of electrostatic phenomena in multivalent electrolyte (divalent and trivalent electrolyte) in the case of biological softmatter, focusing essentially on the interactions of DNA, membranes and proteins. The keynote talk by Dr Serge Lemay showed the nontrivial relationship between electrophoretic data, structure and interactions in the case of DNA in multivalent electrolyte solution (divalent and trivalent electrolyte) and the failures of the present models to explain experimental data. The talks by Profs. Korolev and Mazur showed promising simulation results for the understanding of DNA electrostatic interactions with using different techniques (all atomic, multiscaling) but the relation between the conclusions of simulation results and experimental results is still controversial. In this case, the need for better forcefields and better simulation techniques allowing the simulation of larger time scales was clear. The simulation of electrostatic interactions of membrane lipids with proteins and membrane lipids with multivalent ions, was discussed in the talks by Drs Lorenz and López-Cascales. In these cases, all-atomic molecular dynamic simulations have been able, perhaps surprisingly, to identify the previously unknown mechanisms of lipid selectivity by polypeptide residues and the formation of structures and domains in lipid membranes. The mechanisms suggested by simulations are now being tested experimentally and the first results suggest an excellent agreement between experiments and simulations. Prof. Déjardin discussed the importance of electrostatic interactions in the interpretation of adsorption data of proteins at interfaces and showed how statistical mechanical

models are able to predict this effect correctly. Overall, it can be said that the recent developments in new simulation techniques, forcefields and theories in the case of membranes, lipids and proteins are providing powerful tools which allow us to understand in deep many controversial issues in biophysical interactions. It is also clear that the underlying physics in the important case of DNA electrostatic interactions is still far from being understood. The rationalization of the experimental results obtained with new nanotechnological devices clearly requires the development of new simulation approaches.

4) ***Specific ion effects***

Colloid an interface science is full of experimental evidence for specific ion effects (for example the so-called Hoffmeister series) which are still lacking a theoretical explanation. Models developed by different researchers include completely different physical origins such as the structure of water around charged interfaces and macromolecules (for example, some ions are suggested to be structure-breakers for water), polarization of ions and dispersion forces beyond the standard Lifshitz theory, quantum effects,... Profs. Beattie and Netz explained in their provocative reviews the different points of views in current research. Prof. Beattie discussed in detail the experimental evidence arising from adsorption experiments (for example surface tension measurements) and colloidal stability (including the controversial issue of emulsions stabilized by structured water). Prof. Netz reviewed the evidence from molecular dynamics simulations (both at classical and Car-Parrinello levels). Prof. Vaknin showed also that the evidence from surface sensitive X-ray scattering experiments is in many cases in contradiction with the interpretation given to the experiments using more classical techniques (surface tension, colloidal stability) and also with some molecular dynamic simulations. The main conclusion from the talks and also the poster contributions devoted to this topic is that at the present time we do not understand the interplay between water and ions at charged interfaces. Different sources of information (simulations, surface sensitive X-ray scattering, surface tension, electrophoresis,...) give different perspectives of the problem which seem to be contradictory. During the discussion at the workshop, several lines of research were proposed. In the case of simulations, it is clear that current MD techniques are not appropriate to deal with realistic models of interfaces. Proposed lines of research were the inclusion of ionization and polarization of water and ions at interfaces. It is also clear that simulation results are an essential tool for the interpretation of experimental results at a molecular level. It is also clear that the development of an appropriate molecular interpretation (based on simulations) is essential to solve and understand the contradictions between experimental results coming from different techniques.

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

As stressed by many participants, this event has been unique in his character of bringing together and promoting discussion between scientists from different backgrounds (different experimental techniques, different simulation techniques) and fields (materials science, chemistry, colloidal and interfacial science, biophysics, biochemistry, nanotechnology and nanoscience). Discussion and debate was intense (and sometimes even hot and passionate). Anecdotal evidence showed that some participants extended their stay beyond the workshop to allow for further discussion at the Hotel Campus during the Saturday morning following the event. Also, we were told by several participants (who showed opposite points of view in their talks) that they ended up sharing transportation to the airport and continuing discussion until the very last minute.

This event has allowed scientists working on simulations to be fully aware of the different range of experimental techniques and the different (and in some cases contradictory) pieces of information which can be obtained in the lab with the newly developed techniques such as surface sensitive X-ray techniques, optical tweezers technology and electrophoretic effects in nanodevices. Also, it has allowed experimentalists to discuss and understand the role of simulations and the importance of a molecular interpretation of the experimental results coming from different techniques. In more detail, the main outcome of the workshop consists of:

- Recommendations for the effects and details which need to be accounted for in future developments of new simulation methodologies. Comparative analysis of computational methods and models used in softmatter (colloids, membranes, DNA) in contact with electrolyte solution: Montecarlo simulations of simplified models, mesoscopic methods (Lattice-Boltzmann), all-atomic classical molecular dynamics, Carr-Parrinello calculations.

- Recommendations for the basic ingredients to be included in the development of new theoretical approaches for the understanding of the behavior of softmatter in electrolyte solution.

- Recommendations for new “smoking gun” experiments in order to isolate the key mechanisms essential in the understanding of the behavior of softmatter in electrolyte solution.

- Contacts and possible future collaborations between experimental and theoretical (simulation) groups working in the field.

In summary, this event gave the new-born softmatter community the opportunity to built a common target in the foreseeable future.

Annexes to the Final Report

Workshop "Electrostatic Effects in Soft Matter: Bringing Experiments, Theory and Simulation Together"

- Final Program
- Final List of Participants
- Book of Abstracts

ESF WORKSHOP ELECTROSTATIC EFFECTS IN SOFT MATTER: BRINGING EXPERIMENTS, THEORY AND SIMULATIONS TOGETHER

Day 1: April 10

8:00-9:00 Registration at ICMAB Registration Desk

9:00-9:30 Welcome address at ICMAB Lecture Theater ("Sala d'actes")

Fundamentals (ICMAB "Sala d'actes")

9:30	**Johannes Lyklema**, *Overcharging: the chemistry and physics of it*
10:15	**Roland Kjellander**, *Many-body correlations and effective charges in electrolyte systems*

11:00 to 11:30 *Coffee break*

Fundamentals (ICMAB "Sala d'actes")

11:30	**Alex Travesset**, *Correlations, surface charges and overcharging*
12:00	**Francesc Mas**, *Electrostatic and specific binding to polyelectrolyte ligands*
12:30	**Jan Forsman**, *Equilibrium interactions between charged surfaces immersed in a polyelectrolyte solution*
12:50	**Alberto Martín-Molina**, *Charge inversion and one component plasma models: a monte carlo simulation study*.

13:10 -15:15 **Lunch** with **Poster Session** at **Matgas Hall (Matgas building)**

Electrostatics and DNA (ICMAB "Sala d'actes")

15:15	**Serge Lemay**, *Charge inversion accompanies DNA condensation by multivalent ion*
16:00	**Nikolay Korolev**, Modelling DNA packaging in chromatin
16:20	**Alexey Mazur**, *Ion Dynamics and Water Percolation Effects in DNA Polymorphism*

16:40 to 17:10 *Coffee break*

Electrostatics of biological softmatter (ICMAB "Sala d'actes")

17:10	**Christian D. Lorenz**, *Hydrogen bonding and binding of polybasic residues with negatively charged mixed lipid monolayers*
17:40	**Per Hansson**, *Volume transition and phase coexistence in polyion networks interacting with oppositely charged macroions*.
18:00	**Philippe Déjardin**,*Streaming potential as a function of protein surface coverage*
18:20	**José J. López-Cascales,** *When phospholipid bilayers and air/water monolayers match in behaviour. A Molecular dynamics simulation Study*.

ESF WORKSHOP ELECTROSTATIC EFFECTS IN SOFT MATTER: BRINGING EXPERIMENTS, THEORY AND SIMULATIONS TOGETHER

Day 2: April 11

Ions at liquid interfaces (ICMAB "Sala d'actes")

9:00	**James Beattie**, *Ubiquitous hydroxide ions at hydrophobe/water interfaces*
9:30	**Roland Netz**, *Charged surfaces, water structure and ion specificity*
10:00	**David Vaknin**, *Determination of ion distributions at charged liquid interfaces by synchrotron X-ray scattering studies.*

10:30 to 11:00 *Coffee break*

Colloids (ICMAB "Sala d'actes")

11:00	**Roque Hidalgo-Álvarez**, *Charge reversal in real colloids: Experiments, theory and simulations*
11:45	**Ignacio Pagonabarraga**, *Electrohydrodynamic modelling: from colloids to proteins simulations*
12:15	**Jordi Esquena**, *Interaction Forces Between Latex Particles Stabilized by a hydrophobically Modified Inulin Surfactant*
12:45	**Dani Duque**, *Surface interactions mediated by grafted chains*
13:05	**Martin Trulsson**, *Simulations of latex particles immersed in dendrimer solutions.*

13:25 to 15:00 **Lunch** with **Poster Session** at **Matgas Hall (Matgas building)**

15:00 **Discussion / Round Table at Matgas Lecture Hall (Matgas building)**
with H. Lyklema, R. Kjellander, S. Lemay, R. Hidalgo-Álvarez and A. Travesset.
Moderator: Jordi Faraudo (ICMAB-CSIC)

17:00 **Closure**

Final List of participants

Surname	Name	University/Intitution
Bastos	Delfi	Universidad de Granada, Spain
Beattie	James	University of Sydney, Australia
Benavente Herrera	Juana	Universidad de Málaga, Spain
Calero	Carles	ICMAB-CSIC, Spain
Campos	Lourdes	Universitat Politècnica de Catalunya, Spain
Camuñas	Joan	Universitat de Barcelona,Spain
Carrick	Alexandra	John Wiley and Sons, UK
Cordomí	Arnau	Universitat Politècnica de Catalunya, Spian
Czolkos	Ilja	Chalmers University of Technology, Sweden
Déjardin	Philippe	Université Montpellier 2, France
Duque	Daniel	Universidad Autónoma de Madrid, Spain
Eeman	Marc	Gembloux Agricultural University, Belgium
Esquena	Jordi	IIQAB-CSIC, Spain
Faraudo	Jordi	ICMAB-CSIC, Spain
Forsman	Jan	Lund University, Sweden
Franzese	Giancarlo	Universitat de Barcelona, Spain
Garcés	Josep Lluis	Universitat de Lleida, Spain
Gernandt	Jonas	Uppsala University, Sweden
Guàrdia	Elvira	Universitat Politècnica de Catalunya, Spain
Hansson	Per	Uppsala University, Sweden
Hidalgo-Álvarez	Roque	Universidad de Granada, Spain
Ibarra Armenta	José Guadalupe	Universidad de Jaén, Spain
Jin Xu	Quan Quan	Universitat Autonòma de Barcelona, Spain
Kjellander	Roland	Göteborg University, Sweden
Korolev	Nikolay	Nanyang Technological University, Singapore
Lemay	Serge	Kavli Institute of Nanoscience, The Netherlands
López-Cascales	José Javier	Universidad Politécnica de Cartagena, Spain
Lorenz	Christian D.	King's College, UK
Lyklema	Johannes	Wageningen University, The Netherlands
Madurga	Sergio	Universitat de Barcelona, Spain
Martínez Rodríguez	María	IIQAB-CSIC, Spain
Martín-Molina	Alberto	Universidad de Granada, Spain
Mas	Francesc	Universitat de Barcelona, Spain
Mazur	Alexey	Institut de Biologie Physico-Chimique, Paris, France
Miras Hernández	Jonathan	IIQAB-CSIC, Spain
Netz	Roland	Technische Universitaet Muenchen, Germany
Pagonabarraga	Ignacio	Universitat de Barcelona, Spain
Pegado	Luís	Lund University, Sweden
Porasso	Rodolfo Daniel	Universidad Politécnica de Cartagena, Spain
Puzenko	Alexander	The Hebrew University of Jerusalem, Israel
Reyes	Arfaxad	Universitat Politècnica de Catalunya, Spain
Sala	Jonàs	Universitat Politècnica de Catalunya, Spain
Sanz-Navarro	Carlos	CIN2-CSIC, Spain
Stenhammar	Joakim	Lund University, Sweden
Subirana	Juan Antonio	Universitat Politècnica de Catalunya, Spain
Travesset	Alex	Iowa State University, USA
Trulsson	Martin	Lund University, Sweden
Vaknin	David	Ames Laboratory, USA
Vega	Lourdes	ICMAB-CSIC & MatGas, Spain
Wernersson	Erik	Göteborg University, Sweden