

Final Report

Surfactant Templated Porous Materials: Synthesis and Characterisation

Organizers

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1. Summary (up to 1 page)

Surfactants are molecules composed of a hydrophilic (water-loving) part and a hydrophobic (water-hating) part, which makes them align in water/oil interfaces or form a fascinating range of nanostructures in solution, depending on their concentration, the temperature of the system, and the presence of additives. Materials science exploits the use of surfactants to create self-assembled nanostructures, and good examples range from the synthesis of templated mesoporous silica based materials to the use of surfactants as anchoring points for carbon nanotube frameworks.

Understanding the formation and properties of these materials is a complex task, and although significant progress has been made over the last decade, from experimental, modelling and theoretical perspectives, many issues are not well understood. One of the major challenges that the formation of surfactant templated materials poses is that it is an inherently multiscale problem.

Although an approach for truly multiscale modelling was not discussed in this workshop, the state of the art at different scales, from the role of the surfactant as a catalyst for the silica condensation, to the use of coarse grained models for the description of liquid crystal behaviour, was discussed.

The meeting had 17 participants and 2 organisers from the following countries

Country	Number of participants
France	3
Hungary	1
Ireland	1
Netherlands	2
Poland	1
Portugal	3
Spain	1
United Kingdom	4
United States	3

2. Description of the scientific content of and discussion at the event (up to 4 pages)

In the elaboration of the research proposal we aimed to address a variety of questions that would help us improve our understanding of the formation and behaviour of surfactant templated materials:

1. Ab initio simulations: what can we learn from them with respect to the reaction mechanisms? Which are the stable species in solution? How large are the energy barriers? What is the role of the surfactant? What are the current computational limitations? What is the information that can be transferred to a “many-scale” simulation approach and what is the need for a true “multi-scale” approach?

2. Force fields: which one should we use and how are they parameterised? How transferable are the potentials for different species? How sensitive are the physical properties that determine organic-inorganic self-assembly to variations in the force fields? What information is needed from first principle calculations or experimental data to generate more accurate force fields? What is the trade-off this community is willing to pay between accuracy and transferability?

3. Atomistic simulations: what are the time and length scale limitations? How to deal with reactive systems? Do we know how different are the characteristic time scales for surfactant rearrangements, or exchanges with the bulk and the condensation reaction rates? Which components or species are essential and which can be ignored? How does the formation of alcohols during the silica condensation affect the self-assembled structures? What can we learn from molecular dynamics, Monte Carlo or kinetic Monte Carlo simulations? What is the information that can be transferred to a “many-scale” simulation approach and what is the need for a true “multi-scale” approach?

4. Mesoscopic simulations: Can we really do multiscale simulations for these systems? What is the information that can be transferred to a “many-scale” simulation approach and what is the need for a true “multi-scale” approach? How can we do effective coarsegraining? What are the necessary features that need to be present in a mesoscopic simulation to model the structure and evolution of surfactant aggregates in the presence of condensing silica species? Are hydrodynamic effects important?

5. Characterisation: what features are necessary to understand the properties of the materials? How important is the pore geometry and surface chemistry? What information is obtained from experiments that is useful for modelling methods that are available for the material characterisation?

6. Experimental evidence: what is the simulation community ignoring that experimentalists consider essential? Is it possible to measure properties that would validate simulations at different scales? How can we improve the exchange of information and knowledge?

The content of the meeting partially addressed the questions above and identified those that require more research and evidence before they can be satisfactorily answered. In general, the topics can be divided in 5 sections:

2.1 Quantum calculations

Quantum mechanical calculations can only be performed with a limited number of atoms, but they provide information necessary to decide which is the best representation that one should use for the description of molecular systems.

R. Gomes from U. Aveiro presented results for a variety of silicate species, charged and neutral, indicating how the charges in the oxygen atoms varied depending on the structure of the oligomers and the location of the formal charge. He studied the deprotonation of the silicate systems and provided some insight on the effect of solvation. Parameters obtained from his DFT results were used to develop a potential model for silicates, to be used in atomistic simulations.

Thuat Thanh Trinh from U. Eindhoven showed that the presence of a surfactant template can have an important effect in lowering the energy barrier for the silica condensation reactions. Therefore care must be taken when considering that the surfactant molecules only act as templates, as they can have a catalytic influence in the inorganic polymerisation. This finding can be relevant and probably should be incorporated in the kinetic Monte Carlo simulations that were presented later by C. Ferreiro from U. Edinburgh.

M. Tzonka from the Ecole de Chimie de Montpellier presented quantum calculations for lipid molecules that have an amphiphilic behaviour and can be used as templates for mesoporous biomaterials (scaffolds and drug delivery applications). The role of the different sections of a lipid molecule was discussed, as well as the need for detailed descriptions in classical simulations. A discussion on the comparison with other force fields (CHARMM) indicated that the gel to liquid transition is underpredicted with some force fields, which can seriously affect the estimated stability of self-assembled aggregates.

The work presented by C. Gervais from U Pierre et Marie Curie showed the information on structural properties of silica templated materials that can be extracted using NMR experiments. This was complemented by DFT studies on simple models of silica surfaces. She commented on the potential applications and limitations, and highlighted the importance of developing realistic material structures which can be validated when calculating the shifts observed in NMR. It was discussed that the structures developed at U. Edinburgh and CNRS-Montpellier could be tested to identify the validity of the methods used for their construction.

2.2 Atomistic simulations

Atomistic simulations covered a wide range of aspects, from surfactant self assembly, characterisation of materials by adsorption, to the generation and use of a hypothetical structure database. In this section we summarize the work presented and discussions related to the formation of the materials, while the work that is relevant for the characterisation of the materials will be discussed in section 2.4.

Different aspects of the formation of surfactant templated mesoporous silica structures were presented by M. Jorge from U Porto, B. Coasne from CNRS-Montpellier and C. Ferreiro from U Edinburgh. M. Jorge showed that when silicate ions replace bromide counterions of surfactants, the strong interactions between the silicates and the surfactants lead to the growth of the micelles, followed by their aggregation when silica oligomers are considered. This work sparked discussion on the necessity of atomistic representations of surfactants to describe the synthesis of silica based materials, and on

how the information calculated from molecular dynamics simulations could be incorporated into mesoscopic simulations.

C. Ferreiro showed that kinetic Monte Carlo simulations could be used to generate models of mesoporous structures. He described how to create a model for MCM-41 and SBA-2 ignoring the details and dynamic behaviour of the surfactant aggregates and replacing them by a solid cylinder or sphere, depending on the desired structure. The advantages of this method for the generation of an atomistic model of the material were discussed, and its limitations - specifically the need for *a priori* knowledge of the mesoscopic structure - were addressed. B. Coasne presented briefly the method used in the group of K. Gubbins to generate atomistic models of mesoporous materials. It differs from the work presented by C. Ferreiro as the porous structure is carved out from a solid cristobalite block and does not account for the condensation reaction, but can generate significantly longer pores than the kMC method. Both materials provide a realistic representation of some properties observed in real mesoporous silicas.

A completely different aspect of the use of Monte Carlo simulations was presented by M. W. Deem from Rice U, who described how his group has constructed a database of hypothetical zeolite structures, retaining only those structures that are energetically stable based on a comparison with the structure of quartz. The database contains approximately 450,000 structures, but only about 180 have been identified experimentally. The use and mining of the database for useful structures was discussed, as well as the identification of potential templates for the structures predicted by the database that are not yet synthesized. The sensitivity of the database to substitution of silicon atoms by other T-atoms was addressed in the discussion, as well as the potential location of ions and their importance in separations and catalytic applications.

2.3 Mesoscopic simulations

The presentations on mesoscopic simulations included the design of surfactant-directed carbon nanotube assemblies by H. Bock from Heriot-Watt U, surfactant templated mesoporous silicas by A. Patti (U Utrecht) and F. Siperstein (U Manchester), formation of silica nanoparticles by P. Monson (U. Massachusetts), and modelling the behaviour of liquid crystals using very simple representations by D. Cleaver (Sheffield Hallam U).

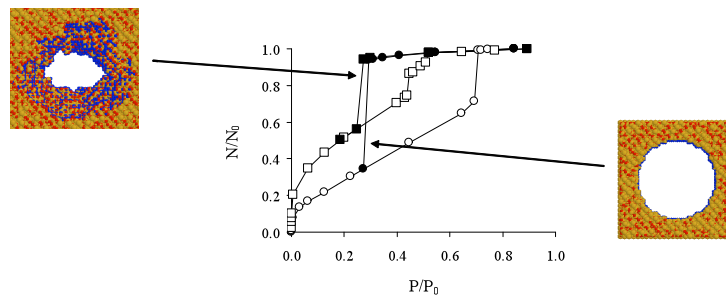
Significantly different descriptions of surfactants or templating molecules were used in the works presented. H. Bock, A. Patti and F. Siperstein used chain molecules with hydrophobic and hydrophilic segments to describe the surfactants. D. Cleaver used solid bodies of different shapes (ellipsoid and pear-shaped) and with variable potentials to account for attractive and repulsive regions in the molecule, while P. Monson used individual lattice sites where the structure directing agent will sit and prevent the growth of nanoparticles.

Discussions included the methods for selecting coarse-grained parameters (including estimated based on atomistic simulations), the sensitivity of the results to the selection of such parameters, techniques to analyse the simulation results and challenges in the area.

2.4 Characterisation of materials

B. Coasne from CNRS-Montpellier and A. Neimark from U Rutgers discussed different approaches that account for surface roughness when modelling adsorption in mesoporous materials. They both highlighted that pores with the same average diameter from a geometrical point of view but with different roughness will have a different capillary condensation pressure, causing rough pores to sometimes be mistaken for smaller smooth pores (see figure below).

Discussions were centred at the interpretation of experimental measurements of adsorption isotherms and the misleading information that is extracted if the pores of the material are smooth. It was highlighted that more work needs to be done to understand the effect of surface heterogeneity at different scales (e.g., atomistic roughness, pore corrugations, distribution of pore sizes, etc.).



Courtesy of B. Coasne

Other characterisation techniques, such as TEM, XRD and neutron scattering were also discussed, highlighting the information that can be extracted from them and how to reproduce such measurements from simulations.

2.5 Challenges from an experimental point of view

Carlos Rodriguez presented different methods to obtain mesoporous silicas and discussed the challenges and lack of detailed understanding of synthesis processes, which simulations could address and aid the interpretation of experimental evidence. The main topics that were identified are:

- Structural evolution during the synthesis when using water soluble precursors
- Self-aggregation (and synthesis) in the presence of additives changing hydration structure (like THF)
- Mechanism of silica formation when hydrophobic surfactants are used as structure directing agents

3. Assessment of the results and impact of the event on the future direction of the field (up to 2 pages)

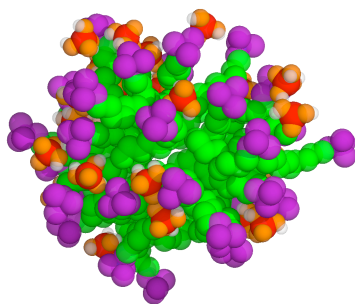
The workshop allowed ample discussion of different aspects that can provide a better understanding on the formation of surfactant templated porous materials, as well as the limitations of different models and methods. More importantly, it provided us with the opportunity to identify points that allow the assessment of the validity of different models.

3.1 Parameterisation of coarse-grained models

Atomistic molecular dynamics simulations presented by M. Jorge showed that short chain surfactants have fairly rigid tails, most of them with all carbon atoms in the trans configuration. This evidence gives confidence that it is valid to model short chain surfactants as rigid objects, like those presented by D. Cleaver. When comparing these two simulations, one with much detail at an atomic level and the other with simple representations of the surfactants but allowing the simulation of sufficiently large boxes to observe the formation of liquid crystals, it was possible to identify which type of parameters can be determined from atomistic simulations when the description of a specific system at a mesoscopic level is desired.

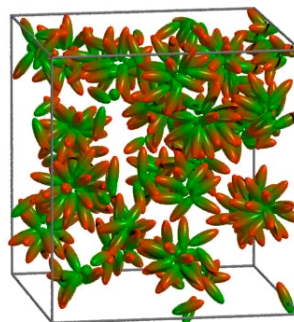
On the other hand, M. Tzonka showed the importance of the chain flexibility in describing surfactants that form bilayer structures when interested in the liquid/gel transitions. This was identified as a possible parameter for parameterisation of mesoscopic simulations.

Molecular simulations



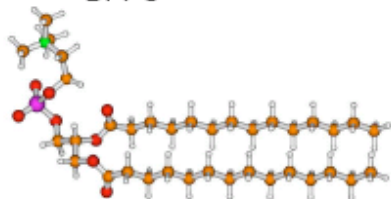
Courtesy of M. Jorge

Mesoscopic simulations

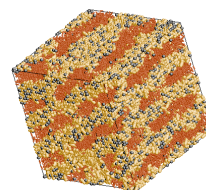


Courtesy of D. Cleaver

DPPC



Courtesy of M. Tzonka



Courtesy of A. Patti

3.2 New methodologies

The development of new methodologies at the mesoscopic level was discussed, including their validity, parameterisation, interpretation and connection with experimental measurements. For example, H. Bock showed simulations using the DPD thermostat but interaction potentials between molecules of the Lennard-Jones type to account for attraction between hydrophobic chains, while F. Siperstein used a modified DPD potential to account for aggregation of silica particles. Advantages and limitations of these methods were discussed.

3.3 Interpretation of experimental data

Experimentally “measured” properties are sometimes obtained in an indirect way, through the interpretation of some truly measured data. For example, pore size is often obtained from gas adsorption isotherms that are analysed using a given model. The necessity of realistic reconstructions of model materials is crucial to test the validity of simple models often used in the interpretation of experimental data. On the other hand, the simulation community needs to gain a better understanding of the experimental techniques, and identify the properties that are truly measured and those that are obtained through interpretation of measured data. It is important to make the community aware that inconsistencies between different experimental techniques can be due to inaccuracies in the models used for their interpretation, and that simulations can help to identify valid models that describe specific phenomena.

4 Final programme of the meeting

Day 1 - September, 10th 2008

13:30 to 14:00 - Registration

13:50 to 14:00 – Welcome (Miguel Jorge)

14:00 to 14:45 - **Jose Richard Gomes**

Molecular Structure and Energetics of Neutral and Anionic Silicates

14:45 to 15:30 - **Thuat Thanh Trinh**

Catalytic Role of Organic Compound in Silica Oligomerization

15:30 to 16:00 - Coffee Break

16:00 to 16:45 - **Christel Gervais**

Combined ab-initio Computational and Experimental Multinuclear Solid-state NMR

Study of a Silica Mesophase and an Amorphous Silica Surface

16:45 to 17:30 - **Tzonka Mineva**

DFT-Based Conformational Analysis and Dynamics of a Phospholipid Molecule (DMPC)

Day 2 - September, 11th 2008

09:00 to 09:45 - **Miguel Jorge**

Molecular Simulation of the Early Stages of the Synthesis of Periodic Mesoporous Silica

09:45 to 10:30 - **Carlos Ferreira**

kMC Simulations of the Synthesis of Mesoporous Silica MCM-41 and SBA-2 Realistic Pores

10:30 to 11:00 - Coffee Break

11:00 to 11:45 - **Henry Bock**

Surfactant Self-Assembly for the Bottom-Up Design of Carbon Nanotube Membranes

11:45 to 12:30 - **Michael W. Deem**

The Monte Carlo Sampling Approach to Construction of a Database of Hypothetical Zeolite Frameworks

12:30 to 14:30 - Lunch Break
14:30 to 15:15 - **Alessandro Patti**
Modeling the Synthesis of Amino-functionalized Mesoporous Materials by Monte Carlo
15:15 to 16:00 - **Doug Cleaver**
Simulation, Characterisation and Analysis of Cubic Phases
16:00 to 16:30 - Coffee Break
16:30 to 17:30 - **Peter Monson**
Modeling Formation of Nanoparticles in Clear-Solution Silicalite Synthesis
17:30 to 18:00 - Discussion
20:00 to 22:00 - Dinner

Day 3 - September, 12th 2008

09:00 to 09:45 - **Flor Siperstein**
Dynamics of Formation of Ordered Mesoporous Materials
09:45 to 10:00 - **Benoit Coasne**
Development of Realistic Models of MCM-41 Materials for Gas Adsorption Studies
10:30 to 11:00 - Coffee Break
11:00 to 11:45 - **Alexander Neimark**
Molecular Models for Adsorption and XRD Characterization of Templated Porous Materials
11:45 to 12:30 - **Carlos Rodriguez**
From Self-aggregation to Nanostructured Solids
12:30 to 14:15 - Lunch Break
14:15 to 14:30 - Closing

5 Participant List

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