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Computer-aided Design of Bio-inspired Nanoporous Silica Materials

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1 Summary

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3 Introduction

Molecular Dynamics (MD) and Monte Carlo (MC) have been powerful tools to simulate molecular interactions of surfactants in solvent systems, allowing a deeper understanding of self-assembly process of this sort of material (Need & Someone, 2025). Therefore, these structural conformations are specially useful to design bio-inspired silica materials (Patwardhan, 2011) since with the addition of silica they remain behaving as scaffolds to mesoporous or nanoporous structures that are maintained even after surfactant removal, silica oligomer polymerization and calcination (Tolbert, Firouzi, Stucky, & Chmelka, 1997). A vast range of silica materials are examples of this phenomena, such as MCM-41 as reported by Kresge and Roth (2013), HR (Jin et al., 2008), MSU-V (Tanev, Liang, & Pinnavaia, 1997) and many others, in which the self-assembly structure depend on the type of surfactant and concentration of the substances involved. Moreover, most of the experimental methods used to obtain data are based on observation and interpretation of final silica structure by using X-ray diffraction (XRD) and transmission electron microscopy (TEM), thus initial self-assembled conformations are predicted as a reflex of the final results and little is known about the mechanistic of this process. However, by using MD simulations it is possible to observe and analyse these initial steps of self-assembly and further predict, with more accuracy, properties and framework provided by surfactant (Tresset, 2009) to generate silica structures.

A major concern is that even though MD uses sophisticated software prepared to simulate enormous systems with thousands of atoms, using all capacities of hardware available, such as high-speed multi-core processors in conjunction with GPUs designed specifically to process data from arrays (Pronk et al., 2013), they hardly can achieve long time horizons and are commonly limited to a few μs depending on the size of the system. For this reason, several techniques have been develop to optimize the performance of the simulations such as coarse-grain models (Need & Someone, 2025). Briefly, the idea behind using this technique is to fit parameters of heavy atoms groups with similar properties in a bigger "bead", which includes atomic masses and electrostatic charges lumped in approximated values. For example, by merging carbon heavy atoms, that means carbon atom and its hydrogen atoms, at a lipid tail in groups of three or four since they have similar hydrophobic properties.

In order to provide topologies to GROMACS simulations several force-fields, for exemple MARTINI (?, ?), use Lennard-Jones potentials fitted to a range of pre-defined bead types to describe coarse-grain models. Furthermore, not only intramolecular beads are possible, but also intermolecular beads can be specified, such as multiple solvent molecules merged in a single bead or ions surround by water molecules. Previous works conducted by (Pérez-Sánchez, Gomes, & Jorge, 2013) with this method recreated a model of surfactant in presence of silica with explicit water that was successful in describing rod-like self-assembly structures detected on MCM-41 materials, demonstrating the capacities of up-scaling this type of systems. Nevertheless, solvent presence demands most of the computational resources, hence implicit solvent scheme has been focus of many studies (Pronk et al., 2013).

Different concepts has been applied to develop a suitable model for implicit solvents, studies conducted by Arnarez et al. (2015) developed the Dry MARTITNI force-field by modifying parameters of its predecessor, in such manner that solvent interactions became incorporated in these values and then solvent beads are no longer necessary. Another method, described by (Mirzoev & Lyubartsev, 2013) is able to recreate a implicit solvent system from interaction potentials generated from a bottom-up approach, that means by using an all-atoms simulation to generate parameters for the coarse-grain model. It is supposed that thermodynamic changes on the system, originated from solvent interaction with amphiphilic molecules, are incorporated on the approximated potentials. Therefore, changes in parameters as concentration may not affect coarse-grained model performance on recreating self-assembly structures (Mirzoev & Lyubartsev, 2014).

The work presented on following experiments are an attempt to create a cross-link method to upscale silica crystal-liquid phase interactions (Tolbert et al., 1997) from the atomistic model to a mesoscale model with the advent of this later coarse-grain technique. The methodology applied to reach the desired model is based on the MagiC software package (Mirzoev & Lyubartsev, 2013) that in conjunction MD simulation software, in this case GROMACS (Pronk et al., 2013), will provide a suitable approximation to self-assembly of amphiphilic molecules in presence of silica. Further explanations of the process are described on Experimental Methods section. For the scope of this project, a bolaamphiphilic molecule 1,12-diaminododecane (DMDD) has been chosen as surfactant because that as seen in previous research by Tanev et al. (1997) it self-assembly in multilamelar vesicles that in presence of a silica precursor is capable of generating a mesoporous structure with remarkable properties. In order to validate this structure formation and further framework formation for silica oligomers, a coarse-grain approximation is suitable option since amphiphilic molecules interaction with solvents can be described efficiently with tabulated Lennard-Jones potentials interactions. As a final

objective at the end of this project, a implicit water coarse-grain model for DMDD will be generated and properly validated based on MD simulations and thermodynamic properties,in order to provide a good approximation to interactions with silica oligomers in a mesoscale model.

4 Experimental Methods

4.1 Theoretical Basis

About gromacs

–MD

Monte Carlo is a simulation method introduced by (?, ?) based on statistical probabilities of a micro-state of a system. Given a canonical system of $\mathcal{N}$ particles, temperature T and volume V it is possible to assume that the free Helmholtz energy of the system A, the internal energy can be described by a group of coordinates, in this case to give a simplified idea assume a distances vector $\vec{r} = (r_1, r_2, \ldots, r_{\mathcal{N}})$ from system origin. for an arbitrary $\vec{r}$ probability a single particle of the system to statistically occupy that position by using a probability distribution function:

–gromacs(van der Spoel et al., 2010)

–MPI and GPU

About MagiC

–General idea

–IBI + IMC

–Parallelism and sample size

–Convergence

4.2 Methods Description

The experimental process of this project is divided in 3 main parts: Firstly, develop a efficient coarse-grain model and validate its use. Secondly, analyse the relationship between concentration of all-atoms simulation and concentration of coarse-grained simulation. Then finally, create and reproduce a Silica surfactant mesoscale system.

In order to maintain standard parameters for all GROMACS simulations, all-atoms simulations that were used for coarse-grained reference were run in NPT ensemble. All simulation boxes were created using genbox (GROMACS package utility), first by inserting the desired number of surfactant molecules and then adding the solvent at the adequate ratio. The molecules were designed based on OPLS-AA forcefield (?, ?) parameters, therefore the surfactant DMDD was created with aid of co-workers and water type was TIP4P (?, ?). Moreover, no initial configuration was determined, such as a pre self-assembled system, to ensure stochastic nature of the system.

Initially, all boxes received a energy minimization step in order to avoid system blow-up deal to possible extreme potential energy spots created during box generation, because due to random displacement of molecules some of them could overlap others and then cause a destabilization of the system. After, an equilibration step was necessary to reach desired initial temperature and pressure conditions for the MD simulation. During equilibration temperature coupling was kept as 298 K using a v-rescaling thermostat (?, ?) with time constant of 0.01 ps and pressure coupling was kept at 1 bar using a Berendsen barostat (?, ?) with time constant of 0.5 ps.

4.3 Experiment 1

–Objective

–Model 1 vs Model 2

–gromacs Simulation Set-up

–MagiC CG M1 and M2 topology generation+Ref RDFs

–IMC process

–gromacs Set-up Reproduction Tests

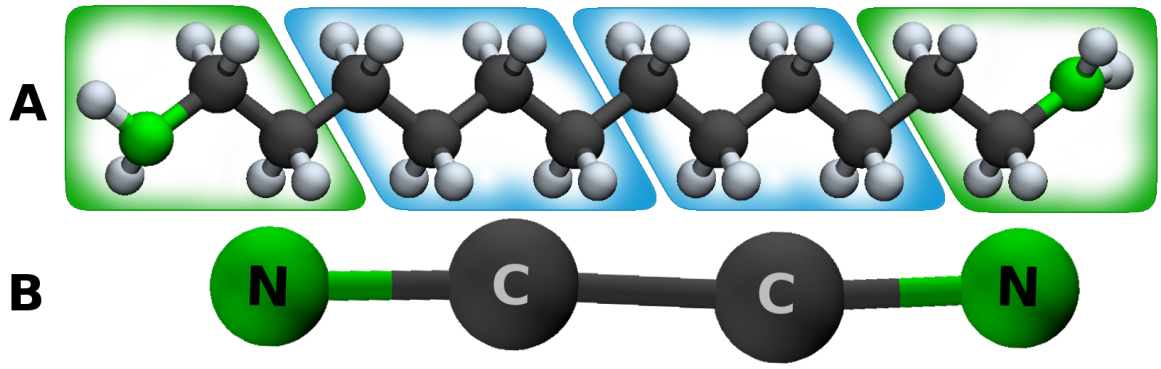

Figure 1: A) Schematic of M1 molecule split plan, Carbon atoms represented in black, Nitrogen in green and Hydrogen in gray. B)Final coarse-grain model for M1. This model aggregated the three most polar heavy atoms on the tips and four apolar heavy atoms at the center. In order to avoid electrostatic interactions on the IMC process and further simulation the heavy atoms groups (heavy atom + hydrogen) were kept thus final charge remain unchanged in each bead

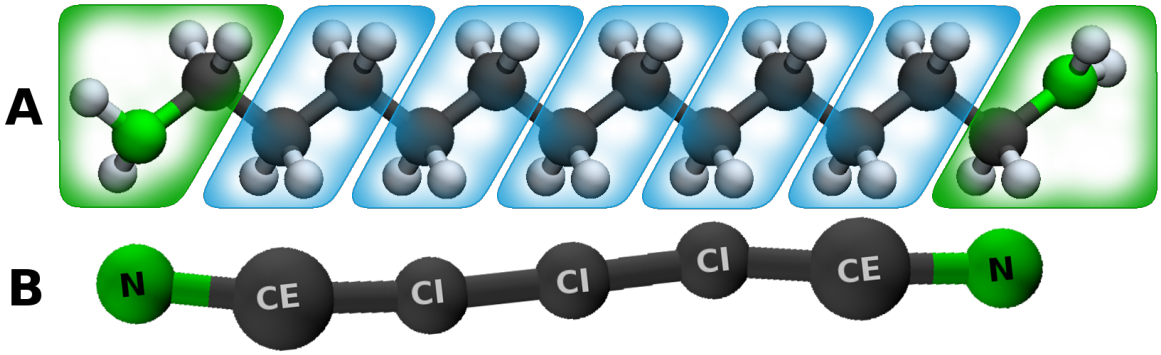

Figure 2: A) Schematic of M2 molecule split plan, Carbon atoms represented in black, Nitrogen in green and Hydrogen in gray. B)Final coarse-grain model for M2. Heavy atom were grouped pairwise in such a manner that amphiphilic parts were kept as distinct as possible. It is important to notice the necessity of two carbon bead types CE and CI

4.4 Experiment 2

–Objective
–gromacs Set-up Up-scaling
–gromacs Set-up Self-assembly Model X(best)
—-AA Low, CG Low
——1k(?) up-scale @ low
——1k(?) up-scale @ high
—-AA Ideal, CG ideal
——1k(?) up-scale @ low
——1k(?) up-scale @ ideal
——1k(?) up-scale @ high
—-AA High, CG High
——1k(?) up-scale @ high
——1k(?) up-scale @ high

4.5 Experiment 3

–Silica addition
—-MagiC CG silica topology
—-gromacs Set-up Self-assembly Model X + Si
——1000, 10000 (Maybe more?)

5 Results

Experiment 1
–Model 1 vs Model 2
–gromacs Simulation
–IMC process Convergence
–gromacs Reproduction Tests RDFs and Properties
Experiment 2
–Self-assembly vs concentration Model X
—-Ideal con validation: Low, Ideal, High con comparison
——Ideal @ Low -> validate
——Ideal @ Ideal -> evaluate
——Ideal @ High -> validate
—-Extremes evaluation:
——Low @ Low vs High @ Low -> compare
——High @ High vs Low @ High -> compare
Experiment 3
–Silica addition
–CG silica Properties
–Self-assembly Model X + Si
——1000, 10000 (Maybe more?)

6 Discussion

Experiment 1
–Which is the best Model?
–Why Model X is better than Model Y?
–To what extent Model X represent well the AA model?
–What are the limitations and advantages of Model X?
Experiment 2
–What is the relation between the entropy "error" and concentration?
–Is the concentration really an problem?
–Do you need to run an AA for each con or the Ideal can represent any?
–Even extreme cases can be approximated? In this case how much is the "error"?
Experiment 3
–Is The silica CG model suitable?
–Can you the proprieties validate it?
–The self-assembly behaviour change with silica addition?

7 Conclusion

What did you really see from the results?
There was any bad assumption that is contestable?
What will be the next step to your research?

8 Nomenclature

H	Hamiltonian hdasdgfag (Mirzoev & Lyubartsev, 2013)a asdfasdfas dfadsfasdfasdfsdfa gsdfhg as djfg ajdf jasdfj adjhg asdjhgfajksdfaj,jahdskjfas
C_n	Molar concentration of species n (mM)

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10 Appendix