

Atomistic Molecular Dynamics Simulation of the CeO₂ Nanoparticle Aggregation

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Abstract - Atomistic molecular dynamics simulation has been performed to study the aggregation of CeO₂ nanoparticles using three different models (neutral, positively and negatively charged) in aqueous solution. For each model, four spherical nanoparticles with 1.0 nm of size were inserted into a box containing 6,900 water molecules and 5 ns of MD simulation has carried out. The preliminary results show that the aggregation occur only in the negatively charged nanoparticle in agreement with experimental data.

How to direct and control the self-assembly (aggregation) of nanoparticles is a fundamental question in nanotechnology. In this way, a detailed understanding of the interactions involved is needed to control the self-assembly. However, the experimental determination of these forces still remains a challenging task. On the other hand, theoretical methodologies such as molecular dynamics (MD) and quantum chemistry can be used to help understand these interactions. Therefore, in the present work, we have used the MD method to simulate nanoparticle aggregation at atomistic level in aqueous solution. We have chosen the cerium oxide (CeO₂) nanoparticle as a model because this metal oxide has several important applications, such as fuel cell electrolyte, catalyst, polishing materials, insulators, gas sensor, UV blockers and others [1]. In addition, the cerium oxide is considered as the most important of rare-earth oxide.

MD simulations were performed in the GROMACS 3.3.3 program [2]. The ensemble NpT (Temperature = 298K and Pressure = 1bar) was considered. Three nanoparticles models: neutral (NN), positively charged (PCN) and negatively charged (NCN) were generated from the crystallographic structure of a cubic fluorite-type of the CeO₂. The size and shape of the nanoparticles were 1.0 nm and nearly spherical form, respectively, were considered. In each model, four nanoparticles with inter-distance of 2.0 nm was inserted into a box (with 5 x 6 x 6 nm of edges) containing 6,900 water molecules. For charged nanoparticles, counter ions were added to keep the system electrostatically neutralized. The Lennard-Jones parameters used here were generated from the Buckingham potential. A total of 5 ns of MD simulation were carried out for each model. Fig. 1 shows the initial configuration and the snapshots obtained at the end of simulation for three models.

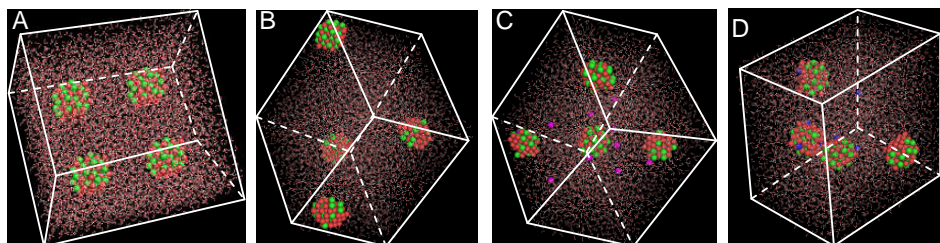


Figure 1. A) Initial model system. Snapshots obtained from the end simulation: B) Neutral; C) positively charged and D) Negatively charged. In balls: oxygen in red, cerium in green, sodium ion in blue and chloride in magenta; water molecules in lines.

Our preliminary results indicate that two nanoparticles in the NCN model began to aggregate. This result is in agreement with experimental data. In this model most of the counter ions (Na¹⁺) are around the nanoparticles interacting via Coulomb and Lennard-Jones interactions. In the NN model it was observed that the nanoparticles are farther than in others models, keeping inter-distance around 4.0 nm. In the PCN model, the distance between three of the four nanoparticles is around 1.5 nm. In all models, the interaction between nanoparticles and water is favorable.

Although we have used small number of nanoparticles and a short simulation time was considered, it shows an important advance in the understanding of nanoparticles aggregation at atomic level. Moreover, this study is necessary to development and to validate parameters for coarse-grained (CG) level. The advantage of the CG model is the possibility to study large systems, e.g. more than 100 nanoparticles in solution, and in large time scale, e.g. microseconds.

References

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Acknowledgments: CNPq and FAPESP