

Theoretical Study of the Colloidal Stability of Metal Oxide Nanoparticles by means of Molecular Dynamics Simulations

O. V. Oliveira⁽¹⁾, A. F. Moura^{(1)*}, and E. R. Leite⁽¹⁾

(1) Department of Chemistry, Federal University of São Carlos, e-mail: moura@ufscar.br

* Corresponding author.

Abstract – We have performed an extensive investigation on the role of molecular scale interactions on the colloidal stability of metal oxide nanoparticles using molecular dynamics simulations. The theoretical calculations give support to the view that the relative strength of different interactions is a key factor determining whether or not coalescence should occur. We also introduce the concept of a theta solvent, similar to the theta condition from polymer science, to show how a stable and yet organized suspension may be obtained.

Molecular dynamics simulations are becoming a valuable investigation tool to understand nanostructured materials. One approach that is frequently used adopts coarse graining schemes for the interactions parameters of the model system, thus simplifying the potential energy landscape while keeping the essential features of the system being studied [1-2]. We report below the findings of a series of molecular dynamics simulations of nanoparticles suspended in liquid media. Each nanoparticle was nearly spherical and had a diameter of 3 nm (the crystalline structure were taken from zirconia, each of the 85 ZrO₂ units being replaced by an interaction site). The overall model system comprised 96 nanoparticles randomly placed within a cubic box (25x25x25 nm) along with 112,320 solvent molecules (each solvent molecule was represented by a single interaction site – this composition matches the typical concentration employed in our experimental investigations). The potential energy surfaces were described by the MARTINI forcefield [3], a coarse grained model originally developed to treat biomolecular systems, but with potential use for inorganic materials as well. We found out that nanoparticles aggregation after (within a timescale of 0.2 μs) strongly depends on the way particles interact with each other and with the solvent. If particle-particle interactions are strong as compared to the particle-solvent terms, the typical structural feature observed resembles a coiled nanowire (Figure 1). If the interactions become isotropic, *i.e.*, particles have the same affinity for each other as for the solvent, a situation similar to the theta condition from polymer science, then different patterns arise. For weakly interacting particles and solvent molecules, particles tend to be more disperse within the liquid medium (Figure 2), whereas strongly interacting particles and solvent molecules give rise to highly organized dispersions (Figure 3). Other parameters schemes have been studied as well, giving a detailed picture of the relations between molecular scale interactions and the overall structural features.

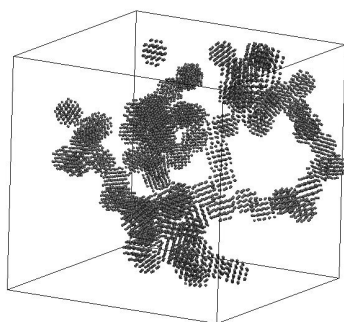


Figure 1 – Final structure (nanoparticles interacting strongly, solvent interacting weakly).

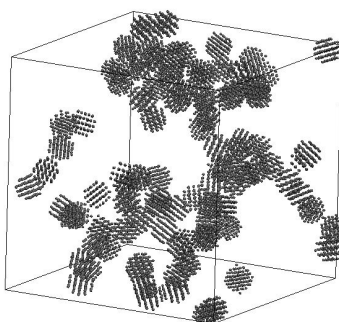


Figure 2 – Final structure (both nanoparticles and solvent interacting weakly – theta condition).

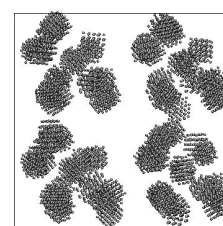


Figure 3 – Final structure (both nanoparticles and solvent interacting strongly – theta condition).

References

- [1] Z. Zhang, M. A. Horsch, M. H. Lamm, and S. C. Glotzer, *Nano Lett.* 3(10) (2003) 1341-1346.
- [2] Z. Zhang, and S. C. Glotzer, *Nano Lett.* 4(8) (2004) 1407-1413.
- [3] S. J. Marrink, H. J. Risselada, S. Yefimov, D. P. Tieleman, A. H. de Vries, *J. Phys. Chem. B* 111 (2007) 7812-7824.