



Molecular dynamics study on iron oxide nanoparticles stabilised with Sebacic Acid and 1,10-Decanediol surfactants



R.A. Harris*, H. van der Walt, P.M. Shumbula

Nanotechnology Innovation Centre, Advanced Materials Division, Mintek, Private Bag X 3015, Randburg, Johannesburg 2125, South Africa

HIGHLIGHTS

- Molecular dynamics calculations of Fe-O nanoparticles with DD and SA ligands are done.
- The degree of stability of Fe-O nanoparticles with ligands DD and SA are determined.
- TEM micrographs and XRD patterns of the samples are obtained.
- Theoretical and experimental results are compared.
- For nanoparticles > 2.6 nm, DD surfactants give a more stable state.

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ABSTRACT

By using molecular dynamics in canonical ensemble (constant atom number, volume and temperature (NVT)) the adsorption of Sebacic Acid (SA) and 1,10-Decanediol (DD) respectively onto the surfaces of an iron-oxide nanoparticle is simulated. The nanoparticle is built by taking into account the inverse spinel structure of a stoichiometric magnetite and the valence of the iron ions ($\text{Fe}_A^{2+}\text{Fe}_B^{2+}\text{Fe}_B^{2+}$ where A and B stand for tetrahedral and octahedral sites, respectively). This study serves to determine theoretically whether surfactants like SA or DD acts as a better stabilising agent for iron oxide nanoparticles of diameters ≥ 2.6 nm. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) measurements on iron oxide nanoparticles stabilised with SA- and DD surfactants were obtained and compared to the simulated results. Unagglomerated nanoparticles with well-defined edges were observed during TEM for DD stabilised particles and a smaller particle size could be calculated for these nanoparticles from XRD patterns. It is concluded that DD stabilises an iron-oxide nanoparticle better than SA because of the difference in the number of oxygen atoms on the respective functional groups.

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1. Introduction

One of the most important and key features of atomic clusters and nanoparticles are that these materials' properties are different from those found under bulk conditions [1]. These properties are strongly dependent upon finite size effects which include among others changes in the average coordination number [2]. For example the average magnetic coordination number is strongly reduced as finite size effects become more pronounced, affecting therefore the magnetic properties [3–5]. The ability of materials to change properties as it approaches the nano-scale holds great promise for new and exciting technological applications [6]. Magnetic nanoparticles have been of great interest because of their extensive applications in high density data storage, biochemistry, hyperther-

mia, *in vitro* and *in vivo* biomedical applications and drug delivery as well as MR contrast reagents [7].

There are still many questions to be answered to understand exactly what happens with materials on the nanometer-scale and this is related to how the different properties of materials evolve as individual atoms are brought together to form nanostructures. A better understanding of this will aid the investigation into the minimum size at which nanoparticles begin to exhibit similar properties as that of the corresponding bulk systems and *vice versa*.

As the chemical bonds between different atoms in nanoparticles as well as between these particles themselves often dominate their properties, nanoparticles are excellent candidates to study the nature of the chemical bond and the influence of the finite-size effects [8]. Iron oxide nanoparticles in particular have attracted much attention because the Fe–O interaction is one of the most important in nature due to the variety of molecules or complexes containing Fe–O bonds and because of their diverse physical and chemical behaviours [9]. The interaction between a substance

* Corresponding author.

E-mail address: richardh@mintek.co.za (R.A. Harris).

and oxygen is one of the most important chemical processes to understand corrosion, biological oxygen transport, and oxide film formation. Well-controlled studies on iron oxide nanoparticles and clusters not only provide a new avenue to obtain detailed information about the interaction between oxygen and iron but also provide models for iron oxide materials [10] and iron oxide surfaces [11].

For practical applications (on the nano-scale) iron oxide nanoparticles (like magnetite) exhibit superparamagnetic behaviour at room temperature, which prevents particle aggregation in the absence of an external magnetic field. Their superparamagnetic property, together with other intrinsic properties, such as low cytotoxicity, colloidal stability, and bioactive molecule conjugation capability, makes such nanomagnets ideal in both *in vitro* and *in vivo* biomedical applications.

Features like structural disorder on the surface when capping the nanoparticles with surfactants increase the complexity of these systems. Fluctuations on stoichiometry are smaller above around 2.6 nm than for particles less than around 2.6 nm in diameter [12], since the system size at around 2.6 nm coincides with that at which the percentage of cations on the surface corresponds to one half the total number of cations. These fluctuations in stoichiometry pose an interesting question as to how these particles would react to different stabilising surfactants that have oxygen atoms as functional groups. It is seldom easy to study small nanoparticles and atomic clusters experimentally as a result of current technological limitations. In this regard theoretical simulations play a key role to study these types of structures. The molecular dynamics (MD) method was first introduced by Alder and Wainwright in the late 1950s to study the interactions of hard spheres [13,14]. The method is now a well-established and important tool that endeavours to simulate the material measurement on an atomistic scale in order to understand the basic origins of material performance. Molecular dynamics (MD) simulations have been successfully applied to predict material properties throughout the last decade. In this study we investigate theoretically, through the aid of molecular dynamic simulations, the stabilising properties of two surfactants (with different oxygen-based functional groups) adsorbed to iron oxide nanoparticles with diameters equal to 2.6 nm. The two surfactants, Sebacic Acid, SA, (with carboxylic acid groups on the peripheries) and 1,10-Decanediol, DD (with hydroxyl groups on the peripheries) are used to stabilise iron oxide nanoparticles. Theoretical simulations for iron oxide nanoparticles with a diameter less than 2.6 nm are reported elsewhere.

2. Theory

To calculate the adsorption density as well as the binding energies of the studied systems, the Monte Carlo method is used firstly. In this computational work, the nanoparticle substrate was loaded with a surfactant mixture of fixed composition, whereupon the lowest energy adsorption sites were determined. The adsorption configurations with the highest probability of occurrence were identified by carrying out Monte Carlo searches of the configurational space of the particle–surfactant system. The temperature was slowly decreased according to a simulated annealing schedule. Since this change in temperature is used to find the optimised geometries and volumes of the nanoparticle–surfactant configuration, the grand-canonical ensemble Monte Carlo (GCMC) technique is not used since it explicitly accounts for density fluctuations at fixed temperature and volume. Also, in the grand canonical ensemble a random choice is made on whether a trial particle *insertion* or *deletion* is attempted. If insertion is chosen, a particle is placed with uniform probability density inside the system. If deletion is chosen, then one out of N particles is randomly deleted. The trial move is

then accepted or rejected according to the usual Monte Carlo rules. A trial move from an original state, O_s , to a new state, N_s , is accepted with probability. Since the loading of all the surfactant components on the particle in this study was fixed in a canonical ensemble the GCMC scheme was not applied here.

A fixed, specified number of surfactant molecules were adsorbed onto a clean substrate. This was done by inserting a random series of steps and equilibration. Moves that changed the loading were excluded to ensure that the loading remained constant. This guaranteed that only the insertion steps that did not create structures with close contact intermolecular interactions and those that passed all the adsorbate location constraints were accepted. The rest were rejected. The candidate particle–substrate configurations were then sampled from this canonical ensemble. The constraints were determined by the “quality” of the calculation which was set to ‘fine’. This means that the number of cycles selected was 5 with 50,000 steps per cycle. A steepest descent algorithm was used with a convergence tolerance of 1×10^{-4} kcal/mol and a force of 0.005 kcal/mol/Å. The displacement was 5×10^{-5} Å and the maximum number of iterations 500. The type of force field used and the charges calculated on the atoms also defined the typical constraints for these simulations and are discussed under Section 2.1 simulation setup.

The molecular dynamics (MD) simulation in canonical ensemble (constant atom number, volume and temperature (NVT)) was then utilised to fully simulate the adsorption of SA and DD respectively onto the surfaces of different sized iron-oxide nanoparticles. The consistent-valence forcefield (cvff) was used which has the following functional form:

$$E_p = \sum_b D_b [1 - e^{-\alpha(b-b_0)}] + \sum_\theta H_\theta (\theta - \theta_0)^2 + \sum_\phi H_\phi [1 + s \times \cos(n\phi)] + \sum_\lambda H_\lambda \chi^2 + \sum_b \sum_{b'} F_{bb'} (b - b_0)(b' - b'_0) + \sum_\theta \sum_{\theta'} F_{\theta\theta'} (\theta - \theta_0)(\theta' - \theta'_0) + \sum_b \sum_{\theta} F_{b\theta} (b - b_0)(\theta - \theta_0) + \sum_\phi F_{\phi\theta\theta'} \cos(\theta - \theta_0)(\theta' - \theta'_0) + \sum_\lambda \sum_{\lambda'} F_{\lambda\lambda'} \times \sum \varepsilon \left[\frac{(r^*)}{r} \right]^{12} - 2 \left(\frac{r^*}{r} \right)^6 + \sum q_i q_j / \varepsilon r_{ij} \quad (1)$$

The minimum binding energies and geometrical configurations was thus determined and further investigated.

2.1. Simulation setup

In the simulation two surfactant chains were sketched using the *Accelrys Materials Studio* software package. A SA surfactant chain is shown in Fig. 1a and a DD surfactant chain with two carboxylic acid groups on the peripheries is shown in Fig. 1b. The DD surfactant chain consists of ten carbon atoms (grey), two oxygen atoms (red) and twenty hydrogen atoms (white), Fig. 1b. The SA surfactant chain (Fig. 1a) also has 10 carbon atoms (grey), but four oxygen atoms (red). Two of the oxygen atoms have a double bond with

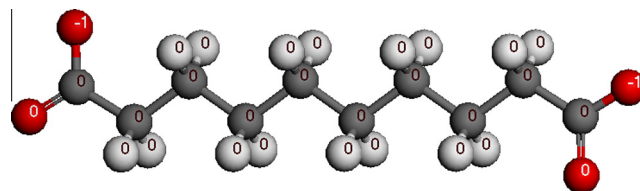


Fig. 1a. Sebacic Acid (SA) surfactant chain. The red spheres represent oxygen atoms, grey spheres represent carbon atoms and white spheres represent hydrogen atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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