

THEORETICAL CHARACTERISATION OF NANOFLUIDS BASED ON METALLIC NANOPARTICLES AND ORGANIC OILS

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ABSTRACT

Equilibrium molecular dynamics simulation was used to model a nanofluid system composed of Cu nanoparticles and organic oils as base fluid (eutectic mixture of diphenyl oxide and biphenyl). The base fluid selected was an experimental fluid used as High Temperature-Heat Transfer Fluid in Concentrating Solar Power (CSP) plants. Thermodynamic properties as heat capacity and thermal conductivity were calculated and the results were compared with experimental data available. The comparison of some properties obtained from our simulated nanofluid system with experimental data let us to validate the model. The analysis of the Radial Function Distributions (RDFs) and the inspection of the Spatial Distribution Functions (SDFs) indicate the important role that plays the metal-oxygen interaction in the system. Dynamic properties as the diffusion coefficients of base fluid and nanofluid were computed according to Einstein relation by computing the mean square displacement (MSD).

INTRODUCTION

One alternative to conventional energy sources is the use of Concentrating Solar Power (CSP) plants. In plants based on parabolic mirrors, a thermal fluid flowing through a tube covered with a coating capable of absorbing radiation is used. The absorbed radiation heats the thermal fluid. Thus, one option to improve the efficiency of these plants is to improve properties of the Heat Transfer Fluid (HTF) usually used. The suspension of solids in liquids can improve some thermal properties of the liquid [1-3]. Specifically, colloidal suspension of some kind of nanostructures, such as nanoparticles, nanotubes, nanofibers, nanorod, in a base fluid is known as nanofluids [4]. An increase of the thermal conductivity of nanofluids based on metallic nanoparticles has been reported [1,2,5-7]. Thus, it is of interest the study of the interactions between the metallic nanoparticles and the HTF used in Concentrating Solar Power plants.

In the present work we report a molecular dynamics study of nanofluids based on Cu nanoparticles and a HTF used typically in CSP plants as the base fluid. This base fluid is a eutectic mixture of biphenyl (C₁₂H₁₀) and diphenyl oxide (C₁₂H₁₀O). The structural properties of these systems were determined by analysing their radial distribution function (RDF) and spatial

distribution function (SDF). The significant thermal properties such as the isobaric specific heat and thermal conductivity were obtained theoretically and were shown to follow the same tendency as values obtained experimentally, which validates the theoretical study method proposed. Our theoretical results indicate the interactions between the Cu and the oxygen from the base fluid play a key role in the structural disposition of the fluid around the metal. That structural disposition can explain the improvement of the thermal properties and the heat transfer coefficient of the Cu-nanofluids compared with the HTF.

COMPUTATIONAL FRAMEWORK

The TraPPE-EH force field [8,9] was used to describe the intra and intermolecular interactions of the HTF fluid (diphenyl oxide/biphenyl Blend). The TraPPE-EH force field treats aromatic rings and the directly connected atoms as rigid entities. The phenyl rings were treated as rigid but were allowed to rotate with regards to each other around the C1-C1' bond of the biphenyls. The metal nanoparticle was described using a Nonbonded Dummy Model [10,11] consisting of six particles, referred to as 'dummy atoms', placed around a central metal particle in an octahedral geometry. The geometry of the dummy complex itself is kept rigid by the imposition of large force constants on the metal-dummy bonds. However, as there are no bonds between the dummy complex and the surrounding ligands, overall rotation of the six-center frame about the nucleus is allowed, and no internal forces are associated with such rotation. Therefore, the coordination geometry is not constrained to the geometry of the dummy model used, but rather, the system is free to exchange ligands.

The TraPPE-EH force field and the Nonbonded Dummy Model use Lennard-Jones (LJ) and Coulomb potentials to represent the nonbonded interactions

$$\mathbf{u}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

where r_{ij} , ϵ_{ij} , σ_{ij} , q_i , q_j , and ϵ_0 are the distance between interaction sites i and j , the LJ well depth, the LJ diameter, the

partial charges on interaction sites i and j , and the permittivity of vacuum, respectively. The Lorentz-Berthelot combining rules were used to determine LJ parameters for unlike interactions.

Molecular dynamics simulations were performed with the DLPOLY code [12] in the canonical ensemble (NVT) using a Nose-Hoover thermostat and periodic boundary conditions. The initial configurations are built with the PACKMOL code [13] providing cubic boxes in which the length of the box sides are chosen to keep the density of the experimental HTF at 298 K (1056 kg m^{-3}). A timestep of 0.5 fs was employed and simulation runs lasted for 1 ns. For the trajectory analysis, structures were saved every 100 timesteps. A cut-off distance of 9 \AA was applied in all the cases and Ewald sum methodology [14] applied to account for the electrostatic interactions.

RESULTS AND DISCUSSION

Based on our experimental results of the characterization of Cu-NFs, we have performed theoretical calculations to gain an insight into the sites of the interaction between the metal and the base fluid in the nanofluid system. The concentration of $5.0 \cdot 10^{-4}$ wt.% for Cu was chosen to ensure the representativeness of the nanoparticle in the nanofluid taking into account the computational cost.

For the Cu-nanofluid system the radial distribution function (RDF) and spatial distribution function (SDF) will be discussed.

The analysis of the RDFs of the Cu-O, Cu-C and Cu-H pairs at different temperatures showed very little variation. Thus, as an example Figure 1 shows the RDFs for the Cu-O pair in the temperature range from 100 to 500 K. In the inset of Figure 1 are included the RDFs at the different temperatures. There are no significant modifications so for the discussion of RDFs and SDFs the trajectories corresponding to the nanofluid systems at 300K were chosen.

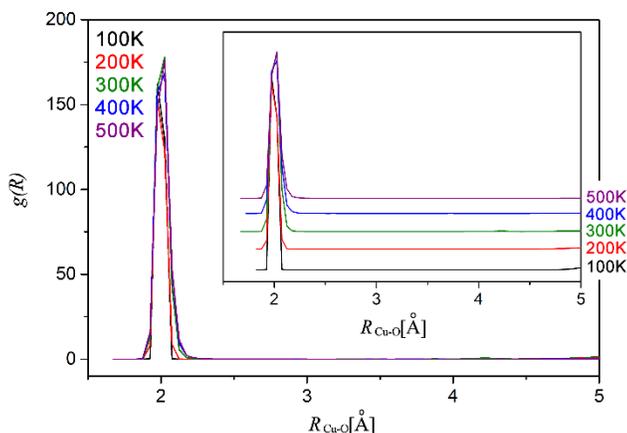


Figure 1 RDF for Cu-O in the range 100-500 K

Figure 2 shows the RDFs at 300K for the Cu-O, Cu-C and Cu-H pairs with the integrations performed up to 6 \AA . The analysis of the RDF of the Cu-O pair (black colour in Figure 2) shows an intense peak centred around 2.0 \AA due to three oxygen atoms that belong to three diphenyl oxide molecules.

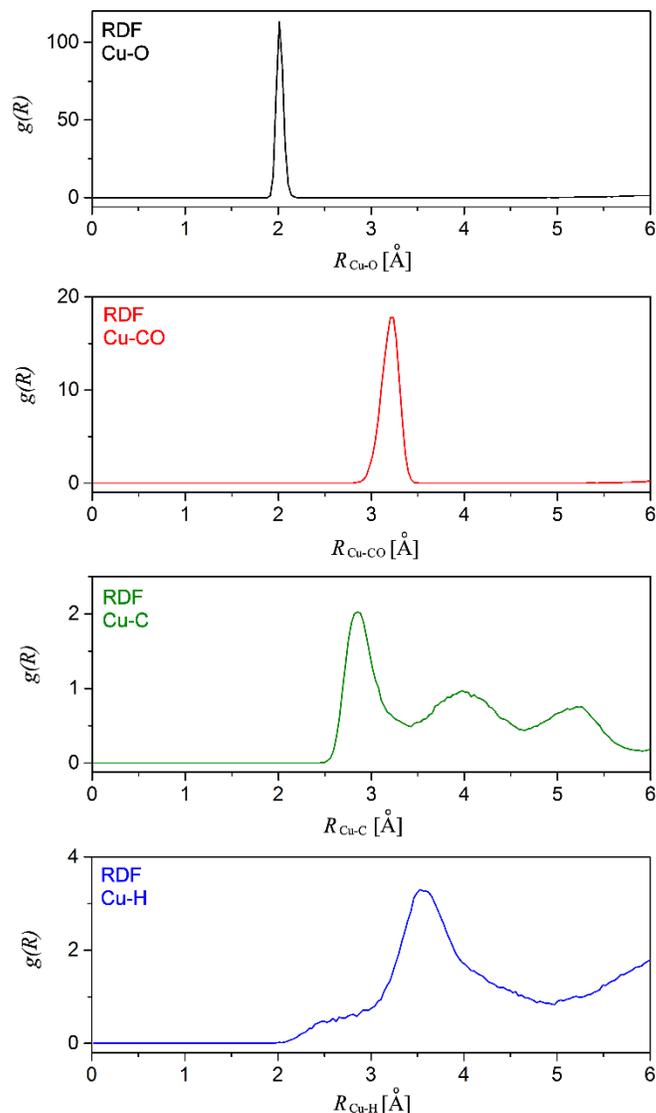


Figure 2 RDF for Cu-O, Cu-CO, Cu-C and Cu-H pairs

For the Cu-C pair, can be distinguished the C atoms linked to the O of the diphenyl oxide (CO) and the ring carbons (C), from the diphenyl oxide and the biphenyl. Thus, there is an intense peak in the RDF of the Cu-CO pair (red colour) at 3.2 \AA attributed to 6 carbons (two carbons for each diphenyl oxide). The RDF of the Cu-C pair (green colour), shows three wide, low-intensity peaks centred at $2.8, 4.0$ and 5.2 \AA that correspond with 6, 17 and 19 C, respectively. Regarding the analysis of the RDF of the Cu-H, a wide band can be seen centred on 3.6 \AA and which corresponds with 20 ring H atoms. It is worth of mention that at distances beyond 5 \AA , a low intensity peak appears for the RDF of Cu-O (6.0 \AA) and another for the RDF of Cu-CO (6.8 \AA), attributed to three O atoms and 6 C atoms, respectively. Therefore, in line with the above, it is reasonable to believe that these atoms correspond to a second layer with three diphenyl oxide molecules

The SDF is an interesting tool to determine how the molecules of the fluid base are arranged around the Cu. Figure 3

shows the SDF for the Cu-nanofluid system in a radius of 3 Å with the Cu in the centre (orange colour). This range was chosen to enable a greater clarity of the image of the first layer around the Cu. The three O atoms (red colour) from the diphenyl oxide molecules are oriented towards the Cu in the centre (orange). The blue coloured spatial distribution corresponds to the carbon atoms linked to the oxygen of the diphenyl oxide (CO). The sky-blue SDFs in Figure 3 correspond to the C atoms of the biphenyl ring whose RDF of the Cu-C pair had 6 C atoms. Thus, the first layer of molecules of the fluid base around the Cu adopts an arrangement with the base of the benzene ring of the biphenyl, the Cu in the centre and three diphenyl oxide molecules around the Cu as depicted in Figure 4, with the O atoms oriented towards the Cu. In Figure 4 the H atoms are hidden for clarity.

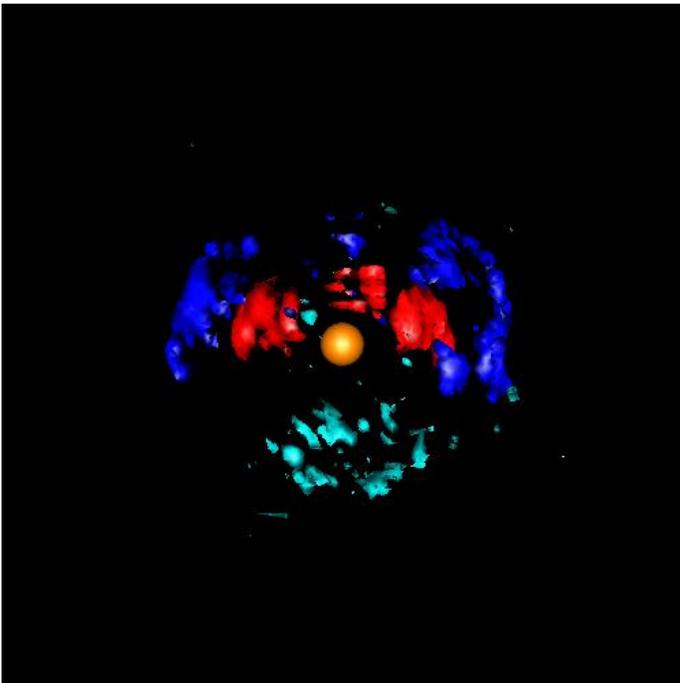


Figure 3 SDFs from the Cu-nanofluid system

A second layer can be seen at 6.0 Å in which another three diphenyl oxide molecules are oriented towards the Cu; Figure 4. The existence of a second layer of diphenyl oxide is interesting because, along with the first layer, it must provide some order to the nanofluid system of the base fluid molecules around the Cu. This may be associated to a greater isobaric specific heat and thermal conductivity of the Cu-nanofluid compared with the base, as will be explained below.

Isobaric specific heat

Figure 5 shows the plot of the total energy of the system versus temperature for both the base fluid and the nanofluids based on Cu nanoparticles in the range of 50 to 500 K. The caloric capacity obtained from the slope of the plots were $2.25 \cdot 10^3$ and $1.94 \cdot 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$ for the Cu-nanofluid and the base fluid, respectively. The values follows the same experimental tendency (data not shown) $C_{p(\text{Cu-nanofluid})} > C_{p(\text{base fluid})}$ obtained in our

laboratory and with the value reported for the base fluid by the supplier. Consequently, as stated above, the Cu-nanofluid system has the most suitable isobaric specific heat value to achieve the most efficient heat transfer processes. This may be because the arrangement of the base fluid molecules around the Cu is favourable for heat transfer processes. The increase of the heat capacity when nanoparticles are incorporated into a HTF has been reported previously [15,16]. But the behaviour found in our nanofluids can be due to a certain internal structure of the base fluid molecules around the nanoparticle, which leads to a positive order of the system [17,18], as previously was stated.

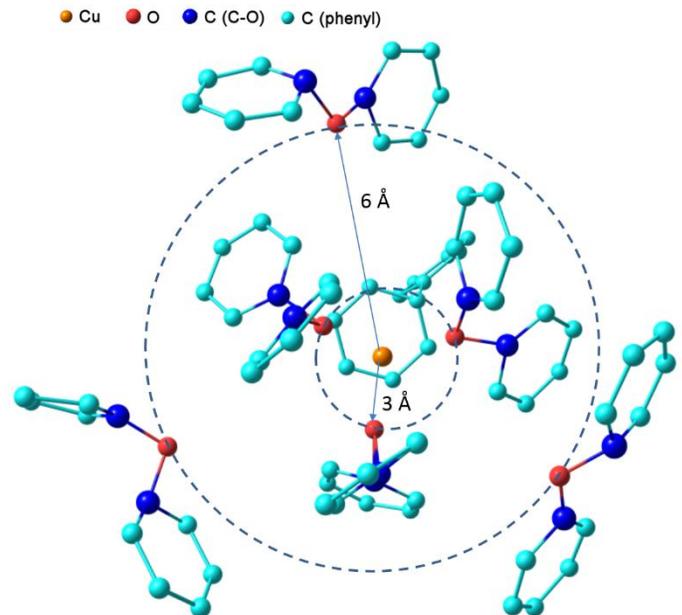


Figure 4 Structure around the Cu in the nanofluid system

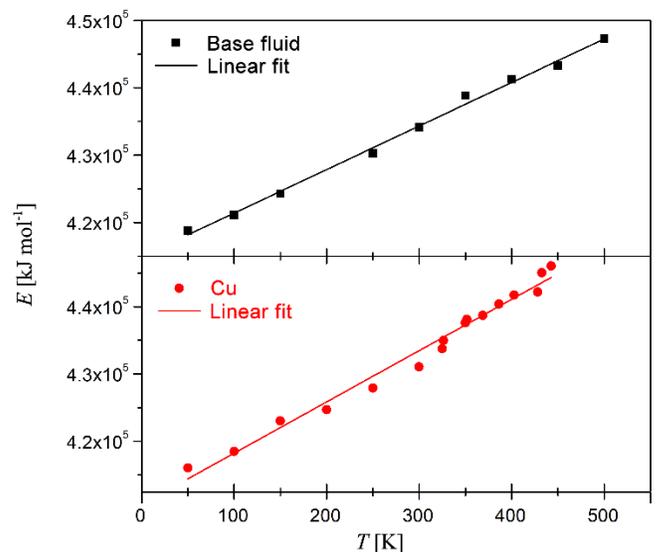


Figure 5 Plot of the energy vs temperature for the base fluid (black) and Cu-nanofluid (red)

Diffusivity and thermal conductivity

The translational diffusion coefficients of base fluid and nanofluids were computed according to the Einstein relation by computing the mean square displacement (MSD).

Figure 6 represents the mean square displacement versus time for the base fluid and the Cu-nanofluid at 300 K, as well as their components in the x, y, and z directions. After approximately 3 ps the mean square displacement varies in line with time for all the systems. The diffusion coefficients are obtained from the slope of this linear relationship. In turn, the thermal conductivity values of the systems analysed was obtained using the diffusion (diffusivity), density and isobaric specific heat values following the equation (2)

$$k(T) = D(T) \cdot C_p(T) \cdot \rho(T) \quad (2)$$

where k is the thermal conductivity, D the thermal diffusivity, C_p is the isobaric specific heat and ρ is the density. The values obtained were 0.147 and 0.107 W m⁻¹ K⁻¹ for the Cu-nanofluid and the base fluid, respectively. The highest value corresponds with the thermal conductivity of the Cu-nanofluid following the same experimental tendency when comparing with Cu-nanofluid obtained in our laboratory and with the value reported for the base fluid by the supplier; that is $k_{(\text{Cu-nanofluid})} > k_{\text{Base fluid}}$.

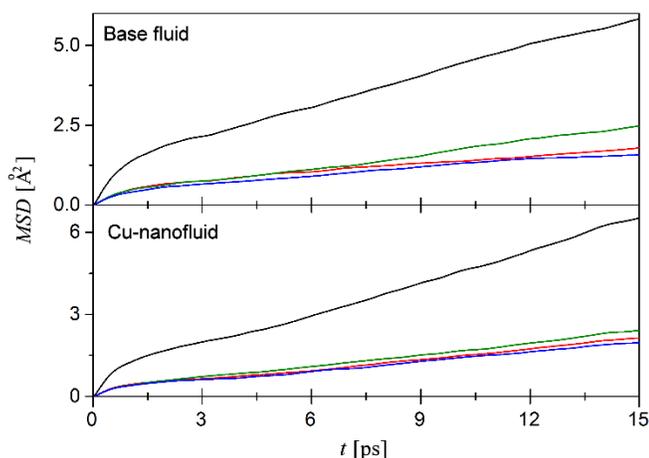


Figure 6 Plot of the mean square displacement (MSD) vs time for the system modelled. The MSD components in the x, y and z directions are shown in red, green and blue colour, respectively

CONCLUSION

In this work, the performance of nanofluids based on Cu nanoparticles and a eutectic mixture of diphenyl oxide and biphenyl as the base fluid has been analysed from a theoretical point of view. This base fluid is used as a heat transfer fluid in Concentrating Solar Power plants.

The isobaric specific heat and thermal conductivity values obtained by molecular dynamics calculations showed the same tendency as the experimental results for the base fluid and the

Cu-nanofluids. Those results validate our model and let us to conclude that the enhancement produced in the isobaric specific heat and thermal conductivity of the Cu-nanofluid is related to the rearrangement of the base fluid around the Cu. This rearrangement consist on two layers around the Cu. Moreover, the directionality of the oxygen atoms of diphenyl oxide molecules toward the Cu in the layers plays a significant role in the order of the system.

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