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Unraveling the role of the base fluid arrangement in metal-nanofluids used to enhance heat transfer in concentrating solar power plants

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ABSTRACT

A comparative theoretical study of Cu, Ag and Ni nanofluids based on a heat transfer fluid used in concentrating solar power (CSP) plants is presented. The base fluid is a eutectic mixture of diphenyl oxide and biphenyl. The nanofluids based on Cu and Ag enhance thermal properties as thermal conductivity and isobaric specific heat of the systems as compared to the base fluid, while Ni nanofluid present a decrease in those properties. An inner layer of base fluid molecules around the metal were observed in which the interaction of the oxygen atom of diphenyl molecules with the metals play an important role. Thus, there are interactions of three, two, and one diphenyl oxide molecules around Cu, Ag and Ni nanoparticles whose trajectory and internal movements around the metals are analysed. Those analysis shown that the Brownian motion observed in the Cu nanofluid was directly related to its highest thermal properties.

1. Introduction

One of the most interesting alternatives to conventional energy sources nowadays is the use of Concentrating Solar Power (CSP) plants. In this regard, the conversion of solar energy into electricity is of interest and CSP systems play an interesting role as thermal energy converters for being used in electric power generation. Although this technology presents elevated cost compared with conventional energy sources. Thus, there are many lines of research that aim this kind of solar plants. One line for improving the efficiency of the heat transfer processes that occur in CSP plants with parabolic cylindrical collectors is the enhancement of heat transfer fluid (HTF) responsible for storing and transporting the heat generated. The improvement of the heat transfer process that takes place in this kind of plants can lead to an improvement of the global efficiency of the plants. Thus, the use of nanofluids, colloid suspensions of solids in base fluids [1], has been shown to be an interesting option for improving the thermal properties of base fluids used for concentrating solar power. Recent studies have shown that the use of nanofluids improve properties as thermal conductivity, isobaric specific heat [2–5] [6,7] or the heat transfer coefficient [5,8–10] of the base fluids. In addition, recent research on metal oxide nanofluids under the influence of electric and magnetic fields have been shown as an interesting method for studying the heat transfer improvement [11–15]. As well as it is of interest for understanding the behaviour of those nanofluids in presence of magnetic fields [16–20]. Therefore an enhancement of those thermal properties contributes to improving the efficiency of the heat transfer fluid, and nanofluids based on metal nanoparticles have been reported to produce an increase in thermal conductivity [2,5,6,21–25].

In this work, molecular dynamic calculations were performed on metal nanofluid (metal = Cu, Ag, Ni), based on a eutectic mixture of biphenyl ($C_{12}H_{10}$) and diphenyl oxide ($C_{12}H_{10}O$) as the base fluid. The structural properties of these systems were determined by analysing their radial distribution function (RDF) and spatial distribution function (SDF). The structural analysis reveals the important role that plays the interaction between the metals and the oxygen atoms from the diphenyl molecules in the enhancement of the thermal properties. This enhancement is the result of a structural reorganisation at molecular level of the base fluid around the metals. To unravel the structural reorganisation at molecular level, translational distribution functions and internal movements of the metal nanoparticle with respect to its average position in the system were calculated from the simulation trajectory. The obtained results show the role that Brownian motion plays in the studied metal nanofluid systems with highest thermal properties, as specific isobaric heat and thermal conductivity.

2. Computational methods

The intra- and intermolecular interactions of the HTF fluid (diphenyl oxide/biphenyl blend) were described by using the Transferable

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Nomenclature

CSP	concentrating solar power
HTF	heat transfer fluid
LJ	Lennard-Jones
MSD	mean square displacement
P(r)	translational distribution function
P(θ)	orientational distribution function
P(ϕ)	orientational distribution function (Torsion angle)
	RDF, g(R) radial distribution function
SDF	spatial distribution function
	TraPPE-EH transferable potentials for phase equilibria-explicit hydrogen

Symbols

C_p	isobaric specific heat
$k\ (T)$	thermal conductivity
$\rho(T)$	density

Potentials for Phase Equilibria-Explicit Hydrogen force field (TraPPE-EH) [26,27]. The aromatic rings and the directly connected atoms are treated as rigid entities when the TraPPE-EH force field is used. Therefore, the phenyl rings were treated as rigid but were allowed to rotate with regard to each other around the C1-C1′ bond of the biphenyls. The metal nanoparticle was described using a Non-bonded Dummy Model [28,29] 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-centre 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 Non-bonded Dummy Model use Lennard-Jones (LJ) and Coulomb potentials to represent the non-bonded interactions

$$u(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \tag{1}$$

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.

The DLPOLY code [30] was used to carry out the molecular dynamics simulations. The canonical ensemble (NVT) was applied in all the simulations performed by using periodic boundary conditions and a Nose-Hoover thermostat. A cubic box providing the initial configuration was built with the PACKMOL code [31]. The length of the box sides were chosen to keep the density of the experimental HTF at 298 K (1059 kg m^{-3}). The experimental nanoparticle mass concentration chosen to ensure the representativeness of the nanoparticle in the nanofluid was of $5.0 \cdot 10^{-4}$ wt% for Cu, Ag and Ni. The Ewald sum methodology [32] was applied to account for electrostatic interactions using a cut-off distance of 9 Å in all the cases. The simulations run lasted for 1 ns employing a time step of 0.5 fs and the structures were saved every 100 time steps for analysing the trajectory.

3. Theoretical analysis by molecular dynamics

3.1. Isobaric specific heat

Molecular dynamic calculations were performed in order to discover a predictive model of the experimental behaviour of the nanofluids. To calculate the caloric capacity equilibrium, molecular dynamic simulations were performed at different temperatures ranging from *c.a.* 50 to 500 K. Fig. 1 shows a linear tendency for the plot of the total energy of the system versus temperature for the base fluid and the nanofluids based on Cu, Ag and Ni nanoparticles. The isobaric specific heat can be obtained from the slope of these plots (Fig. 1). The values obtained were 1940 ± 36 J kg^{-1} K^{-1} for the base fluid and 2250 ± 52, 2150 ± 106 and 1830 ± 35 J kg^{-1} K^{-1} for the Cu, Ag and Ni-nanofluid, respectively. These values, although slightly higher, coincide quite well with the experimental values and show the same experimental tendency, $C_{p(\text{Cu-nanofluid})} > C_{p(\text{Ag-nanofluid})} > C_{p(\text{base fluid})} > C_{p(\text{Ni-nanofluid})}$. Comparing the isobaric specific heat values obtained for the base fluid and the three nanofluids simulated would suggest that the Cu-nanofluid system has the most suitable isobaric specific heat value to achieve the most efficient heat transfer processes following by the Ag-nanofluid system. However, a decrease in the value for isobaric specific heat was showed for the Ni-nanofluid system. These behaviours are related to the different arrangement of the base fluid around of the nanoparticle, which depend on the metal added as will be demonstrated below in the study of the structural properties of these systems. Therefore, the structural reorganisation of the base fluid molecules around the metal nanoparticle plays an important role, as will be discussed below.

3.2. Diffusivity and thermal conductivity

The translational diffusion coefficients of the base fluid and nanofluids were computed according to the Einstein relation by computing the mean square displacement (MSD). This translational diffusion coefficient is the thermal diffusivity used typically in experimental studies. Thus, the diffusion coefficients were obtained by the following equation:

$$D_i = \lim_{t\to\infty} \frac{\left|\vec{r_i}(t) - \vec{r_i}(0)\right|^2}{6t} \tag{2}$$

where $\langle\left|\vec{r_i}(t) - \vec{r_i}(0)\right|^2\rangle$ is the mean square displacement (MSD).

The mean square displacement versus time for the base fluid and the nanofluids with Cu, Ag and Ni nanoparticles at 300 K, as well as their components in the x, y, and z directions, are showed in the Fig. 2. After approximately 3 ps, the mean square displacement varies in line with time for all the systems. The diffusion coefficients were obtained from the slope of this plot and by applying Eq. (2). The thermal conductivity values were calculated using Eq. (3) from the values for the diffusion coefficient, the density and the isobaric specific heat.

$$k(T) = D(T) \cdot C_P(T) \cdot \rho(T) \tag{3}$$

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 0.107 ± 0.002 W m^{-1} K^{-1} for the base fluid and 0.147 ± 0.003, 0.125 ± 0.006 and 0.097 ± 0.002 W m^{-1} K^{-1} for the Cu, Ag and Ni-nanofluid, respectively. Comparing these values with those obtained experimentally [2,25], they can be said to follow the same experimental tendency. The highest value corresponds with the thermal conductivity of the Cu-nanofluid, followed by the Ag-nanofluid, the base fluid and the Ni-nanofluid; that is $k_{(\text{Cu-nanofluid})} > k_{(\text{Ag-nanofluid})} > k_{(\text{Base fluid})} > k_{(\text{Ni-nanofluid})}$.