Effect of aggregation morphology on thermal conductivity and viscosity of 
$\text{Al}_2\text{O}_3$-$\text{CO}_2$ nanofluid: A Molecular Dynamics approach

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Abstract

CO₂ cooling systems are the wave of the future for industrial refrigeration. CO₂ refrigeration systems is gaining traction in recent years which involves heat transfer between CO₂ and the base fluid. The high viscosity of CO₂ is of interest to the oil and gas industry in enhanced oil recovery and well-fracturing applications. A need arises to improve the thermal conductivity and viscosity of CO₂ to increase the efficiency of these significant applications. Aggregation of nanoparticles is one of the crucial mechanisms to improve the thermal conductivity and viscosity of nanofluids. Since the aggregation morphology of nanoparticles is unclear so far, we have evaluated the stable configurations of the aggregation of nanoparticles by determining potential energy of the different configurations system. In this paper, Green-Kubo formalism is used to calculate the mentioned thermo-physical properties of the different aggregated nanofluids. The nanofluid in this study consists of alumina (Al₂O₃) nanoparticles and CO₂ as a base fluid. Results indicate that the enhancement in the thermal conductivity and viscosity of nanofluid is inversely proportional to the potential energy of the system. The results also mark that various morphologies of the aggregated nanoparticles have different enhancements of thermo-physical properties of the nanofluid. This study is conducive for the researchers to perceive the importance and influence of aggregation morphology of nanoparticles and their stability on the thermal conductivity and viscosity of nanofluid.

Keywords: Al₂O₃-CO₂ nanofluid, Aggregated self-assembly, Thermal conductivity, Viscosity, Molecular dynamics simulation
Nomenclature:

\( k_B \) Boltzmann’s constant (J/K)
\( \varepsilon_0 \) Dielectric constant of vacuum
\( r \) Distance between two atoms (m)
\( \theta \) Angle between two atoms (rad)
\( \sigma \) Interatomic length scale between atom
\( \varepsilon \) Interaction strength (J)
\( \phi \) Potential (J)
\( m \) Mass of the particle
\( T \) Thermodynamic temperature (K)
\( N \) Total number of atoms
\( v \) Velocity of particle (m/s)
\( V \) Volume (m³)
\( k \) Thermal conductivity (W/m*K)
\( \mu \) Viscosity (Pa.s)
\( q \) Partial charge (e)

Subscripts:

\( i,j \) denotes atoms
\( \alpha,\beta \) denotes different types of atom
1. Introduction:

Carbon dioxide has a compelling impact on climate change due to its status as greenhouse gas. Yet climate change is not the only reason for extensive research on CO$_2$. An important area of research aims at reduction in CO$_2$ emissions through sequestration techniques. In enhanced oil recovery (EOR), CO$_2$ is used as a solvent and is an integral constituent in the well fracturing fluid [1,2]. Low viscosity is exhibited by CO$_2$ which leads to low sweep efficiency at reservoir conditions. Instead of displacing oil ahead, CO$_2$ “fingers” towards production wells due to this property. Studies have shown that rate of oil recovery and well fracturing efficiency is improved substantially with increase in viscosity of CO$_2$. Past literature reports that introducing ethanol or toluene or using styrene/fluoroacrylate copolymers are successful methods of increasing CO$_2$ viscosity [3,4].

Moreover, the performance and cost analysis of CO$_2$ as a natural refrigerant has drawn attention of many researchers across the globe as the drift towards environmentally benign refrigerants continues. According to Solemdal et al. [5], CO$_2$ systems have proven themselves highly beneficial over other systems by exhibiting lower energy consumption ultimately leading to better system performance and cost-effectivity. Amongst other thermo-physical properties, thermal conductivity of CO$_2$ is significant in storage and cooling systems in avionics, transport and refrigeration process, petrochemical, textile and other industries [6,7]. Enhancing thermal conductivity of CO$_2$ is therefore of vast relevance. With the advancement in nanotechnology, researchers are attempting to improve the thermal conductivity and viscosity of CO$_2$ to increase the efficiency of these significant applications.

Nanofluids [8] are defined as fluids with suspensions of nanoparticles. In comparison with the base fluids, these are potential heat transfer fluids which, even at very low nanoparticle
concentrations, have exhibited a marked increase in thermal conductivities and viscosities (thermo-physical properties). To understand this anomalous enhancement in the thermo-physical properties of nanofluids, researchers have examined the mechanisms of heat transfer [9-14]. The aggregation effect of nanoparticles, which is one of the mechanisms, has received significant attention in recent literatures [15-20]

Aggregation of nanoparticles are easily observable in experimental settings. Keblinski et al [10] proposed four mechanisms that may explain the aberrant enhancement of thermal conductivity of nanofluids. Feng et al [21] derived a model which showed that the small size of nanoparticles is directly proportional to more aggregations and results in enhanced thermal conductivity. Ruijin Wand et al [20] conducted equilibrium molecular dynamics simulations to calculate the thermal conductivity by Green-Kubo method and concluded that the aggregation of nanoparticles can influence the thermal conductivity of nanofluid greatly. A molecular dynamics study by Sedighi [16] concluded that aggregation can improve thermal conductivity of nanofluid only at fixed nanoparticles concentration. Similarly, Lee et al. [15] observed the aggregation of nanoparticles results in a higher increase of the thermal conductivity of Ar-Cu nanofluid compared to well dispersed nanoparticles. Another investigation of Hong [17] showed us that, gelation aggregation can increase effective thermal conductivity greatly.

Another important thermo-physical property to be accounted for in a heat transfer fluid is viscosity. Since a nanofluid is solid-liquid mixture, the viscosity is also expected to be higher than the base fluid. Numerous studies were done on the enhanced viscosity by well dispersed particles. However, few studies have been done to determine viscosity of nanofluid in aggregated states. Kang et.al. [9] showed that the aggregation of nanoparticles induces a significant enhancement in thermal conductivity of nanofluid, while the increase in viscosity
was shown to be gentle. Duan et. al. [17] carried out an experimental study to see the effect of multi-nanoparticle system on the viscosity and found out that the viscosity increases up to about 60% when compared to the base fluid and attributed this enhancement to the nanoparticle agglomeration. Pastoriza-Gallego et al. [22] studied $\text{Al}_2\text{O}_3$-water nanofluid and indicated that different aggregated structures of the nanoparticles have a determining impact on the viscosity of nanofluids. Garg et al [23] investigated the viscosity of copper nanoparticles in ethylene glycol and found out that the viscosity was about four times of that predicted by the Einstein law of viscosity. A study by Gangpreet et. al. [24], found that with increase in the size of the aggregates, viscosity increased at a faster rate.

To the best of authors’ knowledge, the aggregation effect and its stable configuration in the nanofluid in gaseous phase has not been reported in open literature so far. In this paper, an equilibrium molecular dynamics (EMD) simulation is performed to study the effect of nanoparticle aggregation and stability of the aggregated structures on the enhancement of thermal conductivity and viscosity in nanofluids. The objective of the present work is to quantitatively analyze the influence of aggregation on thermophysical property of alumina-carbon dioxide ($\text{Al}_2\text{O}_3$-$\text{CO}_2$) nanofluid. The current study also investigates the self-assembly of nanoparticles’ aggregate and accounts the stability test using system’s potential energy to reveal the underlying mechanisms of thermal conductivity and viscosity enhancement.

2. Simulation setup and Methodology:

Molecular dynamics (MD) simulations are being increasingly adopted as a tool to perform preliminary assessments of nanoparticle (NP) fluid interactions and determining thermal,
mechanical and other properties of interest. The potential interaction between the atoms was calculated through potential energy function which further estimates the force acting on them. This potential energy function depends on the position of individual atoms present in the simulation domain and was composed of bonded and non-bonded energy interactions. The bonded interaction includes energy stored due to the bond-stretching and angle of bending. The non-bonded interactions are evaluated from the Van der Waals and the electrostatic interactions (eg. Coulombic) are calculated using the Particle Mesh Ewald method [25]. In the present work, gaseous CO$_2$ with a suspension of Al$_2$O$_3$ nanoparticle was modeled in Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The CO$_2$ molecules are represented by the conventional elementary physical model (EPM2) model [26], since it is one of the better models to predict thermodynamic properties. Previous studies [27,28] have shown that flexible models are best for determining CO$_2$ properties and hence in our work, we have used the relatively recent TraPPE_flexible model with Morse potential (instead of harmonic potential used to model CO$_2$ by previous researchers). The intermolecular potential consists of long-range Coulombic interactions, and a shifted and truncated 12-6 Lennard-Jones (LJ) potential (equations (1) – (3)) [29].

$$
\varphi_{ij}^{nb} = \varphi_{ij}^{LJ} + \varphi_{ij}^{\text{Coulombic}},
$$

$$
\varphi_{ij}(r_{ij}) = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right],
$$

$$
\varphi_{ij}^{LJ}(r_{ij}) = \begin{cases} 
\varphi_{ij}(r_{ij}) - \varphi_{ij}(r_{c}) & r_{ij} < r_{c}, \\
0 & r_{ij} > r_{c}
\end{cases}
$$

where $r_{ij}$ is the distance between atoms $i$ and $j$, $\epsilon_{ij}$ and $\sigma_{ij}$ are LJ potential parameters, and $r_{c}$ is the cutoff radius. The cutoff radius of $\sim 4\sigma_{O-O}$ was chosen as ‘k’ and ‘μ’ are almost independent after this distance.
The LJ interaction parameters between different types of atoms were calculated from the Lorentz-Berthlot mixing rule (equations (4) and (5)) [29].

\[ \sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}, \quad (4) \]

\[ \varepsilon_{ij} = \sqrt{\varepsilon_{ii} \times \varepsilon_{jj}}, \quad (5) \]

In our previous study [30], using quantum mechanics, it has been shown that the intermolecular attraction between Al₂O₃ and CO₂ molecules is well characterized by using parameters obtained by LB mixing rule.

The Coulombic interactions are given by equation (6):

\[ \varphi_{ij}^{\text{coulombic}} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}, \quad (6) \]

where \( q_i \) and \( q_j \) are the partial charges on atoms \( i \) and \( j \); and \( \varepsilon_0 \) is the dielectric constant of vacuum.

For the fully flexible model, additional function is used to describe bond stretching Morse potential equation (7) and angle bending of CO₂ equation (8)

\[ \varphi_M(r_{ij}) = k_M \left[ 1 - e^{-\alpha(r_{ij} - r_0)} \right]^2, \quad (7) \]

\[ \varphi_B(\theta_{ijk}) = \frac{1}{2} k_B \left( \theta_{ijk} - \theta_0 \right)^2, \quad (8) \]

where \( \varphi_M \) and \( \varphi_B \) describes the bond stretching by morse potential and angular stretching by harmonic potential; \( r_{ij} \) is the distance between atom \( i \) and \( j \); \( \theta_{ijk} \) is the angle between atoms \( i, j, k \).
$k; \ k_M$ and $k_B$ are the force constant. The non-bonding parameters for the TraPPE flexible model are listed in Table 1.

Table 1: LJ parameters used for carbon-carbon and oxygen-oxygen interaction for several CO$_2$ models. Parameters for flexible models with force constants [27].

| MODELS | $\sigma_{O-O}$ | $\varepsilon_{O-O}$ | $\sigma_{C-C}$ | $\varepsilon_{C-C}$ |
|--------|----------------|---------------------|----------------|---------------------|
|        | (Å)            | (K)                 | (Å)            | (K)                 |
| TraPPe | 3.05           | 79                  | 2.8            | 27                  |

$k_M = 2015.75$ kJ/molÅ$^2$, $\alpha = 2.35$ and $k_B = 1236$ kJ/mol rad$^2$

Atomic interactions within Al$_2$O$_3$ are modeled using two- and three-body interaction potential function which has van der Waals interactions, coulombic interactions, steric-size effects and charge-induced dipole. The three-body interaction potential used is the product of angular and spatial dependent factors which correctly describe bond-stretching and bond-bending characteristics developed by Vashishta et al [31].

Molecular dynamics simulations are performed in the canonical ensemble (NVT) and visualized by Visual Molecular Dynamics (VMD) [32]. The time-step is set as 1 fs (femto-second) in the simulations. This time-step was tested for energy conservation. To validate the simulation method with experimental data, we calculated the thermal conductivity and viscosity of base fluid, i.e. gaseous CO$_2$ at $T = 300$ K and $\rho = 150$ kg/m$^3$ through the Green-Kubo formalism, which gave the validation error of 1.42% and 1.13%. To get an averaged value of the ‘$k$’ and ‘$\mu$’, twelve independent runs were carried out. The Nose–Hoover thermostat was used for maintaining the constant temperature conditions of the system.
The size of the simulation domain having periodic boundary conditions in all the three
directions was varied proportionally to have constant bulk density of gaseous CO$_2$ (150 kg/m$^3$)
and constant volume fraction of 1.94% for all configurations. The two phases (i.e. gas and
solid) present in the domain are grouped separately. Minimization was done to remove close
contacts and thus avoid high potential energy collisions. Sufficient time steps were performed
to achieve equilibrium state for CO$_2$ molecules surrounding the nanoparticle, while keeping the
nanoparticle immobile, which was under the microcanonical ensemble (NVE) and Langevin
thermostat. To achieve equilibrium state for the nanoparticle vice versa was done. Then,
canonical ensemble (NVT) was used for the whole system before switching to NPT. The
pressure and temperature are fixed at 54 atm and 300 K respectively. Then, fluctuation of
autocorrelations was performed under the micro-canonical ensemble (NVE) for data
computation to calculate thermal conductivity and viscosity for each nanofluid system.
Newton’s equations of motion were integrated using the velocity Verlet algorithm [33].

MD method relates the thermal conductivity of fluid to equilibrium heat flow autocorrelation
function through Green-Kubo equation [34], which is written as:

$$ k = \frac{V}{3k_BT^2} \int_0^\infty \langle J(0)J(t) \rangle dt $$

(9)

And $J$ is the instantaneous microscopic heat flux vector given by:

$$ J = \frac{1}{V} \left[ \sum_{j=1}^N e_jv_j - \sum_{\alpha=1}^2 \sum_{j=1}^N h_{\alpha j} \sum_{\beta=1}^N v_{\alpha j} \right] + \frac{1}{2} \left[ \sum_{j=1}^N \sum_{j'=1,j\neq j'}^N r_{jj'} (v_{j'} + F_j) \right] $$

(10)

and $e_j$ represents surplus energy of the atom $j$, which is calculated by:

$$ e_j = \sum_j \frac{1}{2} m_j v_j^2 + \frac{1}{2} \sum_{j\neq j'} \phi_{jj'} $$

(11)
where \( v_j \) is the \( j^{th} \) particle velocity, \( h_\alpha \) is the average partial enthalpy of species \( \alpha \), \( F_{ij} \) and \( r_{ij} \) are the interatomic forces and distance between \( i^{th} \) and \( j^{th} \) particles, respectively, \( N_\alpha \) is the number of particles of kind \( \alpha \) and \( N \) is the total number of particles. Average partial enthalpy is the sum of average kinetic energy, potential energy and interaction potential term, which is given by:

\[
h_\alpha = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} (e_j + r_j \cdot F_j)
\]

To calculate thermal conductivity of multicomponent system, \( h_\alpha \) is an important factor to consider [35,36]. For a pure fluid, \( h_\alpha \) is always zero for a single-component system due to the zero-average velocity, but it is non-zero for multi-component systems. The total energy flux is the sum of energy transfer due to mass flow, boundary (pressure) work, and heat conduction. Since, the objective was to calculate thermal conductivity; only conduction energy flux should be considered. Hence, the term containing \( h_\alpha \) should be subtracted from equation (10) to avoid anomalous high thermal conductivity in multicomponent systems.

MD method calculates the viscosity \( \mu \) of fluid based on Green-kubo formalism by integral of the autocorrelation function of the pressure tensor [34] via equation (13).

\[
\mu = \frac{V}{k_B T} \int_0^\infty P_{\alpha\beta}(0) P_{\alpha\beta}(t) dt, \quad \alpha, \beta = x, y, z
\]

where \( V \) is the system volume, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature. \( P_{\alpha\beta} \) is an off-diagonal \((\alpha \neq \beta)\) element of the pressure tensor, which for an \( N \)-particle system is calculated using equation (14) [37].

\[
P_{\alpha\beta} = \frac{1}{V} \sum_{i=1}^{N} m_i v_{i\alpha} v_{i\beta} + \frac{1}{V} \sum_{i=1}^{N} r_{i\alpha} f_{i\beta}
\]

where \( m_i, v_i, r_i \) and \( f_i \) are mass, velocity, position and force of the atom \( i \), respectively. The first term of equation (14) represents kinetic energy, and the second is the virial term. The atom position, force and velocity information are recorded in each timestep.
3. Results and Discussion:

MD simulation with one particle simulates the case that nanoparticles are always well-dispersed in the base fluid [9] which makes it impossible to simulate the aggregation or collision of the particles. Many researchers have stated that the aggregation of the nanoparticles in the nanofluid is the reason of the enhanced thermal conductivity and viscosity. Therefore, two, three, four, five and six multi nanoparticles were taken in the simulation box with the same particle diameter of 3 nm and the same volume fraction of 1.94%. It was observed in the simulation that no aggregation occurred within the time domain of 8 ns in all the cases. Figure 1 shows the snapshot of two particles in non-aggregating and aggregating state. The initial distance is kept constant for all three, four, five and six nanoparticles as that of two particles system. Figure 2(a) and 2(b) show the thermal conductivity and viscosity of non-aggregating state of nanoparticles and the values obtained from GK formalism are in line with the one nanoparticle case. Therefore, till the time nanoparticles with same diameters do not aggregate, the thermal conductivity ($'k'$) and viscosity ($'\mu'$) of nanofluids depend on the volume fraction of the system.

![Fig 1](image1.png)

(a) Position of nanoparticles t=0 ns  (b) Position of nanoparticles t=8 ns  (c) Position of nanoparticles t=10 ns

Fig 1: Two particles’ system at (a) initial stage, t = 0 ns (b) non-aggregating state, t = 8 ns and (c) aggregating state, t = 10 ns. For clear vision CO$_2$ molecules were not shown.
The simulation time was increased to 16 ns for two particles’ system to see whether the aggregation would happen in the MD simulation. Figure 1 shows that the nanoparticle aggregation took place at about 10 ns. It is computationally not feasible to run such simulations for other cases as they need more simulation time to aggregate. Also, to get an average property via GK formalism, one needs multiple runs which is unrealistic if the simulation time is too large.
3.1 Surface area and aggregation effect on ‘k’ and ‘μ’:

Fig 3: (a) and (b) system with one nanoparticle diameter of 3 nm and system with two nanoparticles of 1.987 nm diameter to calculate the effect of surface area and aggregation separately on ‘k’ and ‘μ’ of nanofluid.

To study the effect of surface area and aggregation individually on ‘k’ and ‘μ’, a 3 nm particle and two 1.987 nm particles were taken with the same volume fraction of 1.94%. Figure 3 shows the two different systems. The simulation was computed for 16 ns to determine the thermo-physical properties of the base fluid with one and two nanoparticles system. Figure 4 shows that till 8 ns the enhancement in the properties is due to the addition of nanoparticle and surface area has a very little effect on the enhanced properties of nanofluid. At about 10 ns, aggregation takes place and leads to enhancement in thermo-physical properties of the nanofluid. This can be attributed to the overlap region in the aggregated area which reduces the equivalent surface area and hence increases the thermal conductivity. The enhancement in viscosity is observed because more stress is required to separate the aggregated structure when shearing takes place. Therefore, a high relative viscosity is observed after aggregation.
Fig 4: (a) and (b) shows the effect of surface area and aggregation on thermal conductivity and viscosity of nanofluid in two particles’ system. For other systems the same has been done and shown in the tabulated form (Table 2).
Table 1: Thermal conductivity and viscosity of pure fluid, one nanoparticle system and two nanoparticles system with and without aggregation.

|                          | Thermal conductivity (W/m.k)\(\times 10^{-3}\) | Thermal conductivity enhancement (%) | Viscosity (Pa.s)\(\times 10^{-5}\) | Increase of viscosity (%) |
|--------------------------|-----------------------------------------------|-------------------------------------|-----------------------------------|--------------------------|
| Pure Fluid               | 25.4                                          | -                                   | 1.725                            | -                        |
| One nanoparticle         | 31.7                                          | 24.8                                | 2.374                            | 37.6                     |
| Two nanoparticles        |                                               |                                     |                                  |                          |
| Without aggregation      | 32                                            | 25.98                               | 2.38                             | 37.97                    |
| With aggregation         | 35.3                                          | 39.12                               | 2.89                             | 67.6                     |

The results of one nanoparticle and two nanoparticles’ case with and without aggregation are shown in Table 1, along with the pure fluid case. These results clearly show that the existence of the nanoparticle aggregation causes a significant enhancement of thermal conductivity and viscosity in nanofluid. The maximum enhancement of 39.12% in thermal conductivity and 67.6% in viscosity has been observed during aggregation compared to two nanoparticles’ system where the enhancement for thermal conductivity and viscosity was 25.98% and 37.97% respectively, before aggregation.

3.2 Stability of aggregation morphology, thermal conductivity and viscosity of systems:

To study the nanoparticle aggregation effect and system’s stability on ‘k’ and ‘\(\mu\)’ of nanofluids, the nanoparticles are initially dispersed in the base fluid just contacting each other. Figure 5(a), 5(b), 5(c) and 5(d) show the different configurations of the nanoparticle clusters in the base fluid (base fluid is not shown to make the clusters clearly visible). It is inconceivable to confiscate all the feasible configurations with increase in number of nanoparticles. It is also
observed that different configurations of the nanoparticle cluster resulted in different ‘k’ and ‘μ’ enhancements in nanofluid which is due to variations in stability of the structures in their aggregated form. The potential energy of the different configurations of the system has been determined to check the stability of the aggregated morphology of nanoparticles. Lower potential energy of the system in each multi nanoparticles’ case determines its stable configuration. Figure 5(a’), 5(b’), 5(c’) and 5(d’) show the potential energy of the system in each configuration case. The triangular geometry in 3 nanoparticles’ case has the lowest potential energy and hence is more stable. Also, the ‘k’ and ‘μ’ are more enhanced when compared to its linear configuration. This suggests that with increased stability of aggregating structure, the thermo-physical properties of nanofluid are more enhanced. In the system of four, five and six nanoparticles; trigonal planar (figure b), tetrahedral (figure c) and trigonal bipyramidal (figure d) aggregating structure were found to be the most stable respectively. Therefore, the ‘k’ and ‘μ’ are more enhanced when compared to other configurations.
(c)
Fig 5: (a) Linear and triangular shape of nanoparticles surrounded by CO₂ base fluid (not shown). (a’) Potential energy vs time to compare the stability amongst the two systems. (b) Five configurations of four nanoparticles’ system. (b’) Potential energy vs time to compare the stability amongst the five systems. (c) Five configurations of
five nanoparticles’ system. (c’) Potential energy vs time to compare the stability amongst the five systems. (d) Six configurations of six nanoparticles’ system. (d) Potential energy vs time to compare the stability amongst the six systems.

To see the self-assembly of the nanoparticles, the computation time was increased to 25 ns. To analyze the transition towards a stable configuration, the simulation was carried out only for three nanoparticles’ system. Figure 6 shows the transformation of linear structure to the more stable triangular structure. Similar transition is expected to be observed in systems with more than three nanoparticles but is computationally costly. Table 2 shows the different structures and its properties in both stable and unstable configurations. It was observed that the enhancement in viscosity is more when compared to that of thermal conductivity in each case. The enhancement in the thermo-physical properties studied in this paper are due to the aggregation of nanoparticles and the stability of structures. It should be noted that these configurations are illustrative rather than conclusive.
Fig 6: Self-assembly of three nanoparticles system from linear configuration to the compact and stable triangular configuration. Transition is shown from t = 0 ns to t = 22 ns.

Table 2: Comparison of thermal conductivity and viscosity in all the possible aggregates of three, four, five and six nanoparticles. The stable configuration in each case is marked with an asterisk (*) and shows the maximum enhancement in the thermo-physical properties compared to their less stable configurations.

| Aggregates | Thermal conductivity (W/m.k)*10^{-3} | Increase in thermal conductivity (%) | Viscosity (Pa.s)*10^{-5} | Increase in viscosity (%) |
|------------|--------------------------------------|-------------------------------------|--------------------------|--------------------------|
| Three nanoparticles | Linear shape | 38.31 | 50.82 | 2.91 | 68.7 |
| | Triangular shape* | 41.12 | 61.9 | 3.11 | 80.29 |
| Four nanoparticles | Linear shape | 37.6 | 48.03 | 2.9 | 68.12 |
| | 3,1 pair separately | 37.91 | 49.25 | 2.94 | 70.44 |
| | 2,2 pair separately | 39.2 | 54.33 | 2.98 | 72.75 |
| | Square shape | 39.96 | 57.32 | 3.01 | 74.5 |
| | Trigonal planar* | 42.41 | 67 | 3.152 | 82.724 |
| Five nanoparticles | Linear | 38.9 | 53.14 | 2.95 | 71.01 |
| | 2,3 linear pair np separately | 39.03 | 53.66 | 2.9 | 68.12 |
| | 2,3 triangular pair np separately | 40.1 | 57.87 | 3.02 | 75 |
| | Tapered | 41.8 | 64.56 | 3.06 | 77.4 |
| | Tetrahedral* | 43.2 | 70 | 3.17 | 83.77 |
| Six-nanoparticles | Linear | 38.2 | 50.4 | 2.93 | 69.85 |
| | 3 np each separated | 39 | 53.54 | 2.86 | 65.79 |
| | 2,4 linear pair np separately | 38.7 | 52.4 | 2.9 | 68.12 |
| | 2np pairs separated | 41.06 | 61.65 | 2.943 | 70.6 |
| | 2np pairs together | 42.1 | 65.74 | 2.98 | 72.753 |
| | Trigonal Bipyramidal* | 42.82 | 68.6 | 3.12 | 80.86 |
To summarize the results in Table 2, a comparison between the non-aggregated systems (before aggregation) of varying particles and the stable structure in the aggregated state (after aggregation) of varying particles for thermal conductivity and viscosity are shown in Figure 7(a) and 7(b). Figure 7(a) and 7(b) shows that the aggregation has a significant impact on the enhancement of thermo-physical properties. A maximum enhancement of 70% in the thermal conductivity and 83.7% in viscosity is observed. Since the volume fraction is kept constant, thermo-physical properties do not depend on the number of nanoparticles but on the stability of aggregating nanoparticles.
Fig 7: (a) and (b) show the comparison of thermal conductivity and viscosity in the non-aggregated with the aggregated state of nanoparticles. Out of the different values within the same system, the stable configuration value of thermo-physical property has been plotted for the comparison with its values in non-aggregated state which is marked with an asterisk in table 2.
4. Conclusion:

MD simulations are performed to study the effect of nanoparticles’ aggregation and their self-assembled aggregated structure on the thermal conductivity and viscosity of Al₂O₃-CO₂ nanofluid using Green Kubo formalism. In the simulation process, two to six nanoparticles were put into the simulation box and no aggregation was observed in the time domain of 8 ns for all the cases; and the results of the thermal conductivity and viscosity for the multi-nanoparticle cases were consistent with the result of the one particle case. The computation time was extended till 16 ns in order to observe aggregation of nanoparticles. This was observed for two nanoparticles’ system at 10 ns. In order to simulate the effect of nanoparticle aggregation on the thermal conductivity and viscosity, nanoparticles that were originally stuck together were dispersed in the base fluid. Results showed that the existence of the nanoparticle aggregation induces a maximum enhancement of 70% in thermal conductivity and 83.77% in viscosity of nanofluid at the volume fraction of 1.94%. Multiple configurations of the nanoparticle cluster will cause varying thermal conductivity and viscosity enhancement in nanofluid. Examination of stability of the aggregates using potential energy analysis showed that potential energy is inversely proportional to the enhancement in the thermo-physical properties since the system is more stable. Finally, there are numerous possibilities of clustering and only a limited number of possibilities of clustering are studied in this paper.
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