Thermal interfacial resistance and nanolayer effect on the thermal conductivity of $\alpha$-Al$_2$O$_3$ - CO$_2$ nanofluid: A Molecular Dynamics approach

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Abstract

Nanofluids are known to have significantly different thermal properties relative to the corresponding conventional fluids. Heat transfer at the solid-fluid interface affects the thermal properties of nanofluids. The current work helps in understanding the role of two nanoscale phenomena, namely ordering of fluid layer around the nanoparticle (nanolayer) and thermal resistance at the interface of solid-fluid in the enhancement of thermal conductivity of $\alpha$-Al$_2$O$_3$ - CO$_2$ nanofluid. In this study, molecular dynamics (MD) simulations have been used to study the thermal interfacial resistance by transient non-equilibrium heat technique and nanolayer formed between $\alpha$-Al$_2$O$_3$ nanoparticle (np) and surrounded CO$_2$ molecules in the gaseous and supercritical phase. The nanoparticle diameter ($d_{NP}$) is varied between 2 and 5 nm to investigate the size effect on thermal interfacial resistance (TIR) and thermal conductivity of nanofluid and the results indicate that the TIR for larger diameters is relatively high in both the phases. The study of the effect of surface wettability and temperature on TIR reveals that the resistance decreases with increase in interaction strength and temperature, but is quite independent at higher temperatures, in both gaseous and supercritical nanofluid. A density distribution study of the nanolayer and the monolayer around the nanoparticle revealed that the latter is more ordered in smaller diameter with less thermal resistance. However, nanolayer study reveals that the nanoparticle with bigger diameters are more suitable for the cooling/heating purpose, as the system with larger diameters has higher thermal conductivity. Results show that the nanolayer plays a significant role in determining the effective thermal conductivity of the nanofluid, while the influence of TIR appears negligible compared to the nanolayer.

Keywords: $\alpha$-Al$_2$O$_3$ - CO$_2$ nanofluid, Thermal interfacial resistance (TIR), gaseous and supercritical CO$_2$ phase, Density Distribution, monolayer and nanolayer.
I. INTRODUCTION

CO₂ is of interest due to its potential as a refrigerant, in enhanced oil recovery, in data centre cooling and is therefore extensively studied. As the thermal conductivity ($k$) of CO₂ plays a vital role in these applications, efforts to enhance the $k$ of CO₂ is of prime relevance. One of the means to improve the thermal conductivity of CO₂ is through the addition of nanoparticles, which makes it crucial to evaluate the properties of CO₂ nanofluids. Nanofluids are defined as fluids with suspensions of nanoparticles of 1-100 nm.\(^1\) Numerous studies have been carried out to determine the $k$ and factors affecting it.\(^2\)-\(^7\) For such solid-fluid systems, there is a resistance at the interface, which can be the possible reason for changing $k$ of nanofluid.\(^8\)-\(^11\) The criterion for collective resistance relative to the flow of heat between solid and fluid is known as thermal interfacial resistance (TIR).\(^12\) The concept of TIR was first introduced by Kapitza\(^13\) in 1941 (also known as Kapitza resistance). Moreover, fluid layering at the solid-fluid interface is also one of the factors suggested by Keblinski et al.\(^14\) for the heat transfer analysis in the nanofluids. For this reason, many researchers, particularly in recent years, have studied the Kapitza resistance and molecular layer to understand their impact on the thermo-physical properties of the nanofluid.\(^15,16\)

Advancements of computational techniques and increasing computing resources have greatly enabled the prediction of material properties using molecular dynamics (MD) simulation. MD has been widely adopted to assess the thermophysical properties of nanofluids and its interactions at the nanoscale,\(^17\)-\(^22\) especially because experimentation is difficult, expensive and time-consuming.

The importance of heat transfer at solid-fluid interfaces has motivated researchers to study thermal interfacial resistance and the nanolayer around the nanoparticle to understand their impact on the nanofluid properties. There are several MD studies on understanding heat transfer at interfaces, and we concisely review some of these reports. Maruyama and Kimura demonstrated that in systems at the nanoscale, thermal resistance at the interface of solid-fluid could not be neglected and has a strong dependence on surface wettability of the solid.\(^23\) Vo and Kim investigated the thermal interfacial resistance (TIR) between water and several metallic surfaces.
(gold, silver, silicon, platinum and copper) in nanochannels using non-equilibrium MD simulations. Their work indicated that the behaviour of water molecules are affected by the interaction strength between solid-fluid at the metallic interfaces, and as a result, the TIR is affected. Lervik et al. examined TIR interfaces between n-decane droplets and water using transient non-equilibrium MD simulations. Their results show that interfacial thermal resistance increases with increased particle diameter. Another study using steady-state non-equilibrium molecular dynamics and equilibrium molecular dynamics (EMD) by Barrat and Chiaruttini revealed that the TIR is strongly dependent on surface wetting. Xue et al. explained the functional dependence of TIR in the form of power and exponential law on solid-liquid strength, respectively, for wetting and non-wetting liquids. Wang et al. using the SNEMD approach examined the influence of nanoscale roughness and wetting on Kapitza resistance at the liquid-solid interface and illustrated that the thermal interfacial resistance decreases with roughness and wetting. Rajabpour et al. in his study shows that the TIR is directionally dependent on the heat flux in hybrid graphene-graphane nanoribbons.

Most of the studies of TIR have focused on surface wetting properties of the solid but very few have examined the effect of TIR on thermal conductivity of nanofluid. Though, literature exists on the role of nanolayer in the enhanced conductivity of the nanofluid, further examination is required to comprehend the properties better. Some of the studies are reviewed below.

Lin et al. studied the effect of nanolayer, and particle diameter on ethylene glycol-based copper nanofluid and results showed that the thermal conductivity increases with an increase in diameter. They suggest that the observed results arise due to the combined effect of nanolayer thickness, nanolayer thermal conductivity and nanoparticle size. Xie et al. results show that the interfacial nanolayer and nanoparticle diameter have a significant role in the overall enhanced thermal conductivity of the nanofluid. Xue et al. studied the role of liquid layering on the liquid-solid interface on the interfacial thermal resistance. Their findings showed that a layering phenomenon is not a potent factor in the thermal transport of nanofluids. However, Khodayari et al. demonstrated that the effect of nanolayer on the enhanced thermal conductivity of the nanofluid is negligible. Results from a study by Wang and Jing show that the effect of the
interfacial layer on the enhanced thermal conductivity of Cu-Ar nanofluid is negligible. Therefore, there is a need to investigate whether nanolayer, TIR or both play a role in effective thermal conductivity of the nanofluid as there is an incongruity in the literature.

To the best of authors’ knowledge, the effect of TIR with varying \( \alpha \)-alumina np diameter has not been reported so far. The objective of this work is to study the effect of np diameter and temperature on TIR and to understand the reason for enhanced thermal conductivity of the \( \alpha \)-Al\(_2\)O\(_3\) - CO\(_2\) nanofluid in gaseous and supercritical phase, more precisely, through the monolayer and nanolayer study. The analysis for monolayer and nanolayer effect on the effective thermal conductivity of the nanofluid has been done by Density Distribution. The paper discusses the simulation setup and procedure at first, followed by the discussion of the results obtained and conclusion at the end.

### II. SIMULATION SETUP AND PROCEDURE

Molecular dynamics (MD) simulations have been widely adopted as a powerful tool to assess the interatomic forces at the nanoscale and determining the dynamics and other properties of the system. The potential energy function used determines the forces acting on the atoms. This potential energy function composed of non-bonded and bonded energy interactions. The non-bonded energy interactions include a shifted and truncated 12-6 Lennard-Jones (LJ) potential (Equations (1) – (3)) and long-range Coulombic interactions\(^{34}\).

\[
\varphi_{ij}^{nb} = \varphi_{ij}^{LJ} + \varphi_{ij}^{coulombic},
\]

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

\[
\varphi_{ij}^{LJ}(r_{ij}) = \begin{cases} 
\varphi_{ij}(r_{ij}) - \varphi_{ij}(r_{c}) & r_{ij} < r_{c}, \\
0 & r_{ij} > r_{c}
\end{cases}
\]
where \( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( \varepsilon_{ij} \) and \( \sigma_{ij} \) are LJ potential parameters, and \( r_c \) is the cutoff radius. The cutoff radius of \(-4\sigma_{O-O}\) is chosen since \( k \) and \( \mu \) are independent of \( r_c \) after this distance.

The LJ potential parameters for different types of atoms are calculated from the Lorentz-Berthelot (LB) mixing rule (Equations (4) and (5))\(^{34,35}\).

\[
\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2},
\]

\[
\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \times \varepsilon_{jj}}
\]

It has been shown in our previous study\(^{35}\) that the parameters obtained by L-B mixing rule for intermolecular interaction between \( \alpha\)-\( Al_2O_3 \) and \( CO_2 \) molecules are well characterised by using quantum mechanics.

The Coulombic interactions are given by Eq. (6):

\[
\phi_{\text{coulombic}}^{ij} = \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}
\]

where \( q_i \) and \( q_j \) are the partial charges on atoms \( i \) and \( j \); and \( \varepsilon_0 \) is the dielectric constant of vacuum. The bonded energy interactions for bond stretching by Morse potential (\( \varphi_M \) in Eq. (7)) and angular stretching by the harmonic potential (\( \varphi_B \) in Eq. (8)) for \( CO_2 \) are used.

\[
\varphi_M \left( r_{ij} \right) = k_M \left[ 1 - e^{-e(ij - \theta_0)} \right]^2
\]

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

where \( r_{ij} \) is the distance between atom \( i \) and \( j \); \( \theta_{ijk} \) is the angle between atoms \( i, j, k \); \( k_M \) and \( k_B \) are the force constant. The \( CO_2 \) molecules are represented by TraPPE flexible model\(^{35,36}\) since it has been shown to be one of the better models to predict thermodynamic properties. The L-J parameters for \( CO_2 \) molecules are listed in Table 1.
Table 1: L-J parameters used for oxygen-oxygen and carbon-carbon interaction for several CO$_2$ models. Parameters for flexible models with force constants\textsuperscript{37}.

| MODELS | $\sigma_{O-O}$ (Å) | $\varepsilon_{O-O}$ (K) | $\sigma_{C-C}$ (Å) | $\varepsilon_{C-C}$ (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$^2$

Two- and three-body interaction potential function are used for atomic interaction within $\alpha$-Al$_2$O$_3$ nanoparticle. The two-body function has Van der Waals interactions, coulombic interactions, steric-size effects and charge-induced dipole. The three-body function describes bond-stretching and bond-bending characteristics developed by Vashishta et al.\textsuperscript{38}

Packmol\textsuperscript{39} is used to randomly place CO$_2$ molecules around the nanoparticle as an initial configuration. Periodic boundary conditions are used with a constant bulk density of CO$_2$ (150 kg/m$^3$) and volume fraction of 1.42% for all the simulations. Minimisation is done to remove close contacts and thus avoid high potential energy collisions. After minimisation, sufficient time steps are performed to equilibrate the system in the microcanonical ensemble (NVE). Then the canonical ensemble (NVT) is used for both systems (gaseous and supercritical phase) before switching to the isothermal-isobaric (NPT) ensemble. The gaseous system is then equilibrated from 300-330 K and 54-66 atm in NPT ensemble. Similarly, the supercritical system is equilibrated from 500-700 K and 129-198 atm in the NPT ensemble. Nose/Hoover thermostat\textsuperscript{40} and barostat\textsuperscript{41} are used to update the position and velocities of the atoms at each time step. Now the temperature of $\alpha$-alumina is raised from 600 - 630 K and 800 - 1000 K in the gaseous and supercritical CO$_2$ by directly rescaling the velocities (Eq. (9)) of $\alpha$-alumina atoms.

$$\frac{T_r}{T_b} = \left(\frac{v_r}{v_b}\right)^2$$  \hspace{1cm} (9)
where $T_r$ is the raised temperature and $T_b$ is the equilibrated temperature of $\alpha$-alumina atoms, while $v_r$ and $v_b$ are the velocities of the $\alpha$-alumina atoms respectively. During thermal relaxation, the temperatures of the $\alpha$-alumina nanoparticle and CO$_2$ molecules are recorded at regular time intervals and further used to calculate TIR.

**FIG. 1.** Schematic diagram of the transient non-equilibrium MD

Figure 1 shows the schematic diagram of the transient non-equilibrium MD heat technique carried out in this paper. Once both the systems in the gaseous and supercritical phases reach its initial thermal equilibrium ($T_{ie}$), an ultrafast thermal impulse given to the nanoparticle raises its temperature while the temperature of CO$_2$ molecules is still at $T_{ie}$. During the thermal relaxation process under the microcanonical ensemble (NVE), the heat dissipation takes place from the np to the CO$_2$ molecules to achieve the final thermal equilibrium of both systems.

MD method relates the thermal conductivity ($k$) to heat flow autocorrelation function through Green-Kubo equation$^{34}$ given by Eq. (10):

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

(10)

where $J$ is the microscopic heat flux vector given by Eq. (11):

$$J = \frac{1}{V} \left[ \sum_{j=1}^N e_j v_j - \sum_{a=1}^2 h_a \sum_{j=1}^N v_{a,j} \right] + \frac{1}{2} \left[ \sum_{i=1}^N \sum_{j=1}^N \sum_{i\neq j} r_{ij} (v_j F_{ij}) \right]$$

(11)
and $e_j$ is the surplus energy of the atom $j$ calculated by Eq. (12):

$$e_j = \sum_j \frac{1}{2} m_j v_j^2 + \frac{1}{2} \sum_{i=j} \varphi_{ij}$$  \hspace{1cm} (12)$$

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 Eq. (13):

$$h_\alpha = \frac{1}{N_\alpha} \sum_{j=1}^{N_\alpha} (e_j + r_j F_j)$$  \hspace{1cm} (13)$$

For nanofluid (a multi-component system), $h_\alpha$ is an important factor.\textsuperscript{42,43} For a single component system (pure fluid), $h_\alpha$ is zero due to the zero-average velocity, but it is non-zero for multi-component systems. The total energy flux comprises the energy transfer due to mass flow, boundary (pressure) work, and heat conduction. Since the objective is to calculate thermal conductivity; only conduction energy flux is considered. Hence, the term containing $h_\alpha$ is subtracted in Eq. (13) to avoid anomalous high thermal conductivity in nanofluids.

III. RESULTS AND DISCUSSIONS

The simulation domain shown in Fig. 2 consists of $\alpha$-Al$_2$O$_3$ nanoparticle of 2 nm diameter surrounded by 618 CO$_2$ molecules (visualised by Visual Molecular Dynamics\textsuperscript{44}) and the other configurations details are shown in Table 2. The temperature decay of different diameters of $\alpha$-alumina np and the increment in CO$_2$ temperature during the relaxation period for both the phases are plotted in Fig. 3. It is observed that the temperature of the np decreases as it dissipates heat to the CO$_2$ molecules. Also, it can be seen that the temperature decay of smaller np diameter is faster than the larger np diameter. The temperature difference between the np and CO$_2$ molecules for all the cases in both the phases is shown in Fig. 4 (best fit of logarithmic decay). The slope of this logarithmic decay is later used in calculating the TIR. Interfacial thermal resistance at the np- CO$_2$ interface is calculated using the lumped capacitance approach\textsuperscript{45} given by Eq. (14),
\[ \tau = \frac{mc_T R_i}{A_{np}} \]  

(14)

where \( \tau \) is a time constant, \( m \) is mass of the np, \( A_{np} \) and \( c_T \) are the specific surface area and heat capacity of the np, respectively while \( R_i \) is the TIR. The time constant is calculated by the inverse of the slope of the logarithmic decay (Fig. 4) to time. The time constant for smaller np diameter is lesser than, the larger np diameter. Hence the temperature decay of smaller np diameter is faster than the larger np diameter. The mass (\( m \)) of \( \alpha \)-alumina np is calculated based on the number of atoms present in each np. The time constant for different diameters of np for both the phases is used to determine TIR between np and \( \text{CO}_2 \) molecules at the interface. In this paper, three different parameters, namely the effect of np diameter, surface wettability and the temperature are taken into consideration to see their impact on thermal interfacial resistance.

FIG. 2. The cross-sectional view of the \( \alpha \)-Al\(_2\)O\(_3\) - \( \text{CO}_2 \) nanofluid with 2 nm diameter under investigation.
Table 2: Details of other configurations used to perform the simulations.

| Nanoparticle diameter (nm) | Box Dimension (Å) | Number of Molecules | Number of α-alumina atoms |
|----------------------------|-------------------|----------------------|---------------------------|
| 2                          | 67x67x67          | 618                  | 510                       |
| 3                          | 100x100x100       | 2054                 | 1665                      |
| 4                          | 134x134x134       | 4940                 | 3940                      |
| 5                          | 167x167x167       | 9564                 | 7710                      |

T = 300 K
P = 54 atm

T = 500 K
P = 129 atm
FIG. 3. Temporal variation of $\alpha$-alumina np temperature and CO$_2$ molecules in gaseous ($T=300$ K, $P=54$ atm) and supercritical ($T=500$ K, $P=129$ atm) phases during NVE production run.

![Graph 1](image1)

FIG. 4. Logarithmic temperature difference (best fit) between $\alpha$-alumina np and CO$_2$ molecules temperature in gaseous and supercritical phases during NVE production run.

![Graph 2](image2)

A. Effect of $\alpha$-alumina np diameter on TIR

The density distribution ($\rho_{\text{max}}/\rho_{\text{bulk}}$) of CO$_2$ molecules at the interface (monolayer) of the solid-gaseous and solid-supercritical phase of CO$_2$ is carried out, as shown in Fig. 5 for different diameters (2-5 nm) of $\alpha$-alumina np. It is observed that the density of CO$_2$ molecules at the interface is high for the np with smaller diameters. As the nanoparticle diameter ($d_{\text{NP}}$) increases, the first peak in the density distribution curve decreases. Hence the monolayer distribution is more ordered for smaller np size. Fig. 6 depicts the values of TIR for different diameters of $\alpha$-alumina np. The thermal interfacial res
istance increases monotonically in both the phases with the $d_{NP}$, which can be attributed to the weak coupling due to vibrational mismatch and to the weak adsorption of larger diameter at the interface.

FIG. 5. (a) and (b) show the density distribution of monolayer of CO$_2$ at the interface of 2-5 nm nanoparticle diameter in the gaseous and supercritical phase.

FIG. 6. Effect of nanoparticle diameter on the thermal interfacial resistance in both phases.
B. Effect of Surface wettability and temperature on TIR

As discussed earlier and in our previous study\textsuperscript{35}, the L-J potential function is suitable for the interaction between CO\textsubscript{2} molecules and α-alumina nanoparticle. A parameter $\alpha$ is used to investigate the effects of wettability of α-alumina nanoparticle given by Eq. (15):

$$\alpha = \frac{\epsilon_{pf}}{\epsilon_{ff}}$$  \hspace{1cm} (15)

where $\epsilon_{pf}$ is the inter-atomic interaction energy parameter between np and fluid atoms and $\epsilon_{ff}$ is the intra-atomic interaction energy parameter between base fluid atoms. Different values of $\alpha$ (0.6, 1, 2, 3, and 4) are used to investigate the effects of np surface wettability on TIR in both the phases of nanofluid. Fig. 7 shows the impact of surface wettability on thermal interfacial resistance. The TIR decreases with increasing $\alpha$ in both the phases, but the decrease is more prominent in the gaseous phase than the supercritical phase of nanofluid. This refers that with increasing $\alpha$, the interaction strength increases, which reduces the vibrational mismatch at the np and fluid interface.

![Graph showing variations of TIR with surface wettability (α) of the nanoparticle in both phases.](image_url)
To study the effect of temperature on TIR and surface wettability of the nanoparticle, the nanofluid system with \( d_{\text{NP}} = 4 \) nm is equilibrated at various temperatures. The NVT temperature for gaseous phase is increased from 300-330 K and 500-700 K for the supercritical phase. The calculated TIR as a function of surface wettability and the temperature is shown in Fig. 8. The TIR decreases with the increase in non-bonding strength between solid particle and fluid under a particular temperature, which is concurrent with the existing works of literature.\(^8\)\(^,\)\(^23\)\(^,\)\(^47\) Figure 8 shows the vibrational spectra and modes of CO\(_2\) in the presence of 4 nm particle using Fast Fourier Transform (FFT) of the velocity autocorrelation function (VACF) of carbon and oxygen atom’s velocity. The VACF is calculated by Eq. (16),

\[
C(t) = \langle v(0) v(t) \rangle \tag{16}
\]

where \( v(0) \) and \( v(t) \) are the velocities of carbon and oxygen atoms at \( t = 0 \) and \( t = t \). The values of the velocity auto-correlation are calculated using the inbuilt command in LAMMPS. The amplitude of vibration increases with an increase in temperature, which results in the higher phonon scattering owing to acoustic mismatch at the interface of \( \alpha\)-Al\(_2\)O\(_3\) - CO\(_2\), consequently improving the heat transfer at the interface of solid-fluid. Therefore, TIR decreases with the rise in temperature.
FIG. 8 Vibrational spectra of CO$_2$ with antisymmetric stretch, symmetric stretch and plane bending calculated by carrying out FFT of the velocity autocorrelation function of velocity of carbon and oxygen atoms at various temperatures in the presence of a 4 nm particle.
Figure 9 (a) and 9 (b) also show that the effect of temperature diminishes as hydrophilicity increases. As high surface wettability surfaces increase the collision frequency between solid and fluid at the interface and hence thermal transport dependence on temperature reduces.

FIG. 9 Thermal interfacial resistance as a function of temperature and surface wettability in (a) gaseous phase and (b) supercritical phase.
C. Effect of nanolayer and TIR on the thermal conductivity of nanofluid

The thermal conductivity ($k$) of nanofluid in both the phases and at different temperatures is calculated via Green-Kubo theory with varying loadings of the nanoparticle by keeping the constant volume fraction at 1.42% and bulk density of CO$_2$ (150 kg/m$^3$). To validate the simulation method with experimental data, we calculated the thermal conductivity of gaseous CO$_2$ at $T = 300$ K and supercritical CO$_2$ at $T=500$ K, through the Green- Kubo formalism, which gave the validation error of 1.42% and 1.2%. Fig. 10 compares the $k$ of nanofluid in the gaseous phase at $T = 300$ K and supercritical phase at $T=500$ K at different $d_{NP}$ with the base fluid (no addition of nanoparticle). The $k$ of nanofluid is higher than that of the base fluid in both the phases, and it exhibits an increasing trend with the increase in $d_{NP}$. Density distribution is carried out to see the effect of nanolayer on the thermal conductivity of the nanofluid. Fig. 11 shows the density distribution curve for both the phases at $T=300$ K and $T= 500$K. Observations show that the supercritical phase of CO$_2$ has thicker nanolayer relative to that in the gaseous phase and is attributed to be a reason for the enhanced thermal conductivity of $\alpha$-Al$_2$O$_3$ - CO$_2$ nanofluid. The monolayer distribution indicates that the TIR increases with increase in np diameter, whereas the nanolayer study shows that thermal conductivity increases with an increase in np diameter. This implies that the effect of TIR on the overall enhancement of the thermal conductivity of nanofluid is negligible, and nanolayer formation is one of the reasons for the improvement. The thicker and denser the nanolayer, higher is the enhancement in thermal conductivity.
FIG. 10 Comparison of thermal conductivity of base fluid with different nanoparticle diameter in both the phases at 300 K and 500 K.

FIG. 11 (a) and (b) show the density distribution of nanolayer of CO\textsubscript{2} at the solid-fluid interface of 2-5 nm nanoparticle diameter in gaseous and supercritical phase at 300 K and 500 K.
IV. CONCLUSIONS

The transient non-equilibrium heat technique is carried out using MD simulations to investigate the effect of diameter of $\alpha$-alumina np and surface wettability on TIR between $\alpha$-alumina and CO$_2$ molecules in gaseous and supercritical phases for the first time. MD simulations are also performed to access the effect of TIR and nanolayer on the thermal conductivity of nanofluid. The analysis is done by density distribution of CO$_2$ molecules around nanoparticle in both the phases. It is observed that the thermal time constant decreases with the decrease in np diameter, which leads to lower TIR in both the phases. The monolayer density distribution reveals that the layer at the interface is more ordered for smaller $d_{NP}$ than the bigger $d_{NP}$. Hence TIR is higher for larger $d_{NP}$ nanofluid systems. Also, as the surface wettability of $\alpha$-alumina increases, the TIR shows a decreasing trend. This is because the interaction strength increases with $\alpha$, which reduces the vibrational mismatch at the np and fluid interface. It is observed that the TIR decreases with the increase in temperature and the effect of temperature at high surface wettability is almost negligible. Lastly, the density distribution of the nanolayer study reveals that the impact of TIR on the enhanced thermal conductivity of nanofluid with larger diameters is insignificant. The nanolayer gets denser with larger $d_{NP}$ and is attributed as one of the reasons for the enhanced thermal conductivity of the nanofluid. This study reveals the role of TIR and nanolayer in the improved thermal conductivity of $\alpha$-Al$_2$O$_3$ - CO$_2$ nanofluid. A better understanding of such nanofluids have a significant impact on the potential applications such as enhanced oil recovery, space, nuclear power reactors, and data centre thermal management.

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