Rheological properties of super critical CO_2 with Al_2O_3: Material type, Size and Temperature effect

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Abstract

Super-critical (SC)-CO_2 based nanofluid have been developed to use in oil and gas industry to improve the fluid viscosity and reduce problems with poor macroscopic sweep efficiency in oil reservoirs. In this study, we have studied the effect of aluminum dioxide (Al_2O_3) nanoparticle (NP) on the enhancement of the thickening of SC-CO_2 by characterizing the viscosity and self-diffusion coefficient of the nanofluid. These two properties are highly dependent on the parameters of thermomechanical loading, NP size, NP shape, and NP-based material, which have been studied in detail for relevant temperature (350, 380, and 410) K and pressure 200 bar at 1% volume fraction. As studying the rheological properties of the nanofluid needs an appropriate prediction model, molecular dynamic (MD) is a method of analysis in energy-based applications has been applied to evaluate the enhancement of the rheological properties of the base SC-CO_2 fluid including Al_2O_3 NP. Molecular modeling of SC-CO_2 liquid based nanofluid is challenging to choose generic and accurate force fields to describe the reactions of inter-atomics. In this study, condensed-phase molecular potentials for atomistic simulation studies (COMPASS) force field potential for modeling SC-CO_2 liquid and Charge optimization many body (COMB) force field potential for modeling Al_2O_3 NP and its interaction with CO_2 molecules have been employed. To make the nanofluid more practical, spherical radius NP ranged in size from 1.0, 2.0, and 3.0 nm is used. The results show that the thermophysical properties of the nanofluid are direct proportional to temperature and reversely proportional to NP size. Moreover, NP-based material and NP shape exhibit significant effect of enhancement in the nanofluid properties. The results indicate that spherical shape of Al_2O_3 NP has mainly enhanced the relative viscosity and self-diffusion coefficient of SC-CO_2 liquid in comparison

with the cylindrical CuO NP in our previous study. The viscosity is enhanced almost 3.6 times for smallest NP, also, implementing 1.0 nm Al_2O_3-SC CO_2 nanofluid improves the relative viscosity from 1.94 to 3.59 and then to 3.67 by increasing temperature from 350 K to 380 to 410 K.

Key words: nanofluid, material type, nanoparticle, thermosphysical, viscosity

1. Introduction

Studies on CO_2 injection as an Enhanced Oil Recovery (EOR) method shows a great potential for increase of oil recovery as well as the benefit of sequestering CO_2 in oil producing formations which could be critical component of future greenhouse gas management programs due to the large density difference and also adverse mobility ratio between displacing fluid (CO_2) and displaced fluid (oil).

CO_2 flooding may result in unfavorable displacement efficiency (e.g. channeling, gravity instability) and therefore, poor sweep efficiency.[1,3] An increase in CO_2 viscosity which results in lower CO_2 mobility may reduce problems with viscous fingering and early CO_2 break through which in turn could increase sweep efficiency of the oil reservoir. Therefore, design of an economic CO_2 thickener remains extremely relevant research topic for CO_2-EOR. Efficiency of thickeners such as polymer, foam, and gel has been discussed in previous studies.[4-6] This is shown that surfactant induced CO_2 foam in an effective method for reducing CO_2 mobility; however, the method has some weakness due to long-term stability surfactant loss due to adsorption in porous media results in a larger consumption of surfactant which will affect the economy of the project.

The use of nanoparticles (NPs) instead of surfactant to stabilize CO_2 by forming a nanofluid (NF) may overcome the long-term instability and surfactant adsorption loss and high cost issues that affect efficiency of CO_2-EOR process. However, experimental testing for appropriate

choice of the NP with the required effect on liquid CO_2 viscosity by forming a stable NF is not straight forward and is expensive and time consuming.

In this study, molecular dynamic (MD) modeling is used to study the rheological properties of super critical CO_2 (SC-CO_2) with Al_2O_3 NP. Using especial nanoparticles (NPs) and choosing suitable NP types needs to have understanding micro and macroscale interactions between NPs and fluids.[11] Researchers have focused on different particles' shape and types for enhancing viscosity, thermal conductivity, density, and specific heat. Some of them devoted to investigate thermal conductivity.[12-14] Some researchers have supposed viscosity effects on heat transfer.[15-18] Applications of using nanofluids in lubrication[19], biological[20], oil and gas[21], and chemical industries[2] are the other example of applying these kind of material in industry.

To make the study narrow among vast thermophysical properties of fluids, this study focuses on the viscosity of the fluid which plays a significant role for heat transfer and fluid transport. In our previously published study,[24] we investigated applying CuO NPs in super-critical (SC) CO_2 liquid to increase its viscosity to provide good sweep efficiency in the oil reservoirs. Khaledialidusti et al.[24] stated that nanofluid are mainly characterized by Brownian agitation that can make agglomeration process. So, the crucial point becomes stabilizing nanofluids to have more reliable and appropriate properties. There should be repulsive forces for forming this stabilization between SC-CO_2 and NP and this can be created if a strong mono-layer of the CO_2 molecules absorbs on the surface of the NP. Quantum mechanics (QM) can help to find the surface where the CO_2 adsorption is stronger and give the most promising NP surface for the NP to make the CO_2 based nanofluid.

There are many affords to introduce and suggest different types of nanofluides, but most of them related to NP dispersion in an inert fluid.[5-8] The previous studies on nanofluids were employed the potentials such as Lennard-Jones (LJ), [25] Buckingham,[26] Embeded-Atom method (EAM),[27] Tersoff,[28] and Reactive Empirical Bond Order (REBO).[29] Sankar et al.[6] and Li et al.[5]

investigated a nanofluid system including the L-J potentials. Rudyak et al.[10] worked on aluminum and lithium NPs with liquid argons using L-J potential and they showed the effect of size and material of the NP on the viscosity. Loya et al.[9] studied on CuO NPs in water by using Charge optimization many body (COMB) potential. Rudyak et al.[10] studied the viscosity, thermal conductivity, and heat transfer properties of nanofluids using L-J potential.

To the best of our knowledge, a limited number of studies have been performed by employing hybrid potentials in order to capture none more realistic interatomic interaction between diffusion molecules in nanofluids.

In this study, we employed two force fields, one of them is the condensed-phase molecular potentials for atomistic simulation studies (COMPASS) force field[30] and the other one is the COMB force field. [31-32] In this study, the enhancement of the thickening of SC-CO_2 using the Al_2O_3 NPs is evaluated. Section 2 deals with description of molecular dynamic (MD) method and two force fields are employed in this case study. Section 3 illustrates steps of MD evaluation in NVT and NPT ensembles. Section 4 discusses results and in section 5 makes to conclusion.

2. Computational method

Molecular dynamic (MD) is a method of analysis inert- atomic and inter-molecular interaction in energy-based applications. In this study, the nanofluid is subjected to high temperature and pressure therefor, energies of the atoms dynamically have been changed and to describe this phenomenon, it should be known charge transfer among the atoms of SC-CO_2 liquid and NPs. LAMMPS is a software for Large-scale Atomic/Molecular Massively Parallel Simulator.

It can model atoms and their interactions by using potentials for different stats like solid, liquid, and coarse-grained in parallel technique. There are some tools such as force filed, interatomic potential, and boundary condition for analyzing MD simulation which give the researchers

ability to model sophisticate systems. Having good background of using MD simulation makes easy extend or modify new capabilities using atom types in LAMMPS.[33-34]

Molecular modeling of SC-CO_2 fluid is challenging and requires a careful treatment due to the fairly weak intermolecular interactions. Therefore, to conduct atomistic simulations of SC-CO_2, it is really crucial to apply a generic and accurate force field. Several models have been proposed so far to capture the thermodynamic behavior of the SC-CO_2 liquid. [35-37] however, some of them underestimate the inter-molecular forces in condensed phases.

In this study, COMPASS force field[30] as one of the most reliable potentials which provides an accurate inter-atomic and inter-molecular interactions, especially in condensed phases[30] has been applied for SC-CO_2 modeling at different temperatures. Besides, COMB potential also has been employed to model Al_2O_3 NP and its interactions with SC-CO_2 for some reasons[37]. The main reason is that, interface region consists of bonding and components between an oxide and metal can be different from either the bulk metal or bulk oxide and a force field has to describe different materials besides varying bonding environments at the same time. So, achieving transferability to all phases is crucial work and the solution is properly choosing functional forms.

COMB is applicable to all bond types and able to transfer charge dynamically. In fact, COMB has been put in the category of potential format which has integrated the many body effects into the two-body and in this way, it can dynamically transfer charges of atoms.

In addition, the NPs process in CO_2 is investigated by employing COMB potential. The simulation results reveal that CO_2 molecules can absorb on the NP surface and consequently may change the polar components. Obviously, aggregation may not be happened in the surface of NPs during the process of adsorption by using minimum time step.

The present study deals with effect of Al_2O_3 NPs with fixed volume fraction on the viscosity of SC-CO_2 at different temperatures. In our previous study,[24] we studied the effect of the CuO NP on the viscosity enhancement of SC-CO_2. This study points out the effect of a different metal oxide, Al_2O_3, as well astemperature and NP sizes on this case. So, it is divided into three parts. Firstly, the effect NP size on the CO_2 viscosity is investigated by varying the NP size in the range of (1-3) nm at temperature and pressure of 380 K° and 200 bar, respectively. Secondly, the effect of temperature on the viscosity of SC-CO_2 is evaluated. Thirdly, this study has been compared with the previous study and evaluated effect of NP based-material and shape on the viscosity. This study provides noticeable insights into the thermosphysical behavior of Al_2O_3 NPs in CO_2 liquid.

2.1 COMPASS Force field

COMPASS force field[30] is used to evaluate interatomic interaction. This force filed has been validated for CO_2[3]and also is capable to use for SC-CO_2.[24] It is shown that this force field can be capable of accurately predicting thermophysical properties for broad range of substances including CO_2. COMPASS includes the bonded and non-bonded potential. The bonded potential consists of bond stretching, angular bending, dihedral angle torsion, cross terms and out-of-plane interactions as shown in **Equation 1**. The non-bonded potential is composed of long-range electrostatic interaction and short-range van der Waals (vdW) interaction. The electrostatic interaction is revealed by Coulombic equation and the vdW interaction is represented by 9-6 Lennard-Jones function, which are described by the following equations.

$$E = E_{bond} + E_{angle} + E_{torsion} + E_{oop} + E_{cross} + E_{vdW} + E_{coulomb} \quad (1)$$

$$E_{vdW} = \sum_{i,j} \epsilon_{ij} \left(2 \left(\frac{r_{ij}^0}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^0}{r_{ij}} \right)^6 \right) \quad (2)$$

$$E_{ele} = C\frac{q_i q_j}{\varepsilon R} \tag{3}$$

In **Equations 2** and **3**, the subscripts i and j are pairs of atoms. ϵ_{ij} and r_{ij}^0 are LJ-9-6 parameters given for homatomic pairs. More details of COMPASS force field can be found in the paper published by the developer of COMPASS[30].

2.2 COMB force field

This potential is a powerful available charge potential.[38] The equilibrium charge on each atom is calculated by the electronegativity equalization (QEq) method.

$$\begin{aligned} E_T = \sum_i \Big(& E^{self}(q_i.r_{ij}) + E_{ij}^{Coul}(r_{ij}.q_i.q_j) + E^{polar}(q_i.r_{ij}) + E^{qq}(q_i.r_{ij}) \\ & + E^{qZ}(q_i.r_{ij}) \Big) \\ & + \sum_{j>i} \Big(E_{ij}^{short}(r_{ij}.q_i.q_j) + E^{vdW}(r_{ij}) + E^{corr}(r_{ij}.\theta_{jik}) \Big) \end{aligned} \tag{4}$$

Where r_{ij} and θ_{jik} represent the coordination array of the system and q is the charge array. **Equation 4** involves self-energy of one atom and the coulomb interactions between ion pairs. The self-energy has ionization energy of an isolated ion and can be changed in combination with other atoms in a molecule. So, coulomb energy expresses charge density on each ion. Furthermore, this equation involves the atom polarization E^{polar}, the charge-charge interactions E^{qq}, the charge-nuclear interactions E^{qZ}, vdW interaction, and correction terms to obtain additional physical and chemical reactions in a system. COMB potential also uses several functions such as LJ and E^{field}, influence of filed effects, for vdW interactions. These functions make COMB flexible and realistic in different systems.

2.3 Model Construction

Modeling Al_2O_3 is the first step and the construction of molecular Al_2O_3 is arranged correctly in all atoms method for making interactions of the atoms properly according to their natural

physics. This method of modeling was applied on CuO NP and showed that it is in good agreement with experimental result.[24]

The second step is modeling the system including pure SC- CO_2 which has been carefully examined with the experimental thermo-physical parameters. It is worthily to notice, if vdW potential exists between two atoms, there is an attractive tail at large separation. According to literatures considered a definite cut-off radius of 9 Å essential is order to save computing time.[38]

$$V_T = \sum_i V_1(r_i) + \sum_i \sum_{j>i} V_2^{eff}(r_{ij}) \qquad (5)$$

In this case, calculating triplets of molecules is time-consuming and only considering approximate pairwise is remarkably good. So, **Equation 5** introduces V_2^{eff} as a representative term of different bonds which is applicable for short-range. Also, if coulomb terms are present, there is rising repulsive wall at short distance because of non-bonded overlap between the electron clouds. There are two methods to solve this matter as follows.

In the first method, each ion is a core surrounded by a shell. Electron cloud is situated on the shell part and also is negative and the rest of ion charge is located on the core. The shell and core of a given ion are coupled by a harmonic spring potential and also the shell is taken to have zero mass however, this kind of simulation takes a lot of time.

In the second method, electronic polarization model will be selected based on all aspect of bonding such as breaking and forming bonds which would be captured by using classical harmonic springs. This model involves distortion of the electronic charge cloud belongs to electrostatic field from the other molecules that is known as shell where a polarizable site is represented as a heavy core particles of charge +q and a massless shell particle of charge –q connected with spring constant k. So, this method can be described by choosing the charge-charge interactions of ionic system method wherein the ionic charge induces a dipole on the neighboring ion which makes the last method more reliable and applicable to solve the event.

The unit cell with the dimension of 10 nm is initially filled with CO_2 molecules and different densities depending on the phase behavior parameters (i.e., temperature and pressure). Charge-group-based cutoff are applied for the calculation of the non-bonded interactions for both vdW and electrostatic terms. Particle-particle particle-mesh (pppm) solver[39]is applied each time-step to compute long-range Coulombic interactions. The tail corrections are also added for the vdW interactions using neutral groups. [40] The cutoff value is considered usually in a range of 9.0 and 10.0 Å in all cases. In this study, COMPASS functional follows **Equation 6** in detail.

$$E_{total} = \sum_{b}(k_2(b-b_0)^2 + k_3(b-b_0)^3 + k_4(b-b_0)^4) \sum_{\theta}(k_2(\theta-\theta_0)^2 + k_3(\theta-\theta_0)^3 + k_4(\theta-\theta_0)^4) + \sum_{b,b'} k_{b,b'}(b-b_0)(b'-b_0{}') \quad (6)$$

Where there are some constants are given in **Table 1-3**. There are several terms such as bond stretching, angle deformation, cross-coupling of bond-bond and bond-angle, and non-bonded terms.

Table1: Atom-atom interaction parameters for CO_2[30]

Atom	$r_0(A^\circ)$	$\varepsilon_0(Kcal/mol)$
C	3.915	0.068
O	3.360	0.067

Table2: Bond Increment[30]

Atom		$\delta_{ij}(A^\circ)$
i	j	
C	O	0.40

Table3: Bond and Angle[30]

	Bond Coefficient				
Atom					

i	j	$\delta_{ij}(A^{\circ})$	$b_0(A^{\circ})$	k_2	$k_3(\frac{\text{mol}}{\text{Kcal}})^{1/2}$	$k_4(\frac{\text{mol}}{\text{Kcal}})$
C	O	0.40	1.16	1161.34	-2564.57	3932.87
		Angle Coefficient				
i	j	k	$\theta_0(\text{deg})$	k_2	k_3	k_4
O	C	O	180.00	57.10	0.00	0.00

3. MD simulation

MD is a computer simulation method to study the physical movement of atoms and molecules in order to calculate the physical and chemical properties of systems. Depending on the systems, they sometimes are huge and need to be computed for long time. Since the MD calculations are time-consuming and because of the limited computer memory, the systems have to be represented explicitly in a computer model. The common approach is based on the periodic boundary conditions. Also, the Verlet algorithm[41] is usually used in MD simulations. Velocities can be calculated from the positions or propagated explicitly as in alternative velocity Verlet schemes. The velocity Verlet method with a 1 fs time step for the pure SC-CO_2 system and a 0.2 fs time step for the SC-CO_2 system including the Al_2O_3 NP has been applied as the integrator in all simulations. The accurate force calculation on the atoms is required to update velocities in the stepwise. So, they have implemented to account for all types of atoms. As mentioned above, choosing proper potential is debatable to capture thermophysical properties.

In fact, we have molecular modeling of a complex system involving different types of bonds. So, it is necessary to find a method which considers all aspects to overcome this sophisticated model. To solve that it will be considered the electron density calculation by using some solution method like Density Functional Theory (DFT) and MD. However, DFT is quite computationally expensive for the scale of the nanostructures in spherical NP shape.

There are some atomic force field can describe this physical system which have been developed to obtain the overall effects of the electronic degrees of freedom. These force fields provide ability to expand the horizon of the complexity. The interactions have been proceeded by potential $U(r_1. \ldots . r_N)$ as the function of their positions $r_i = (x_i. y_i. z_i)$. The force on i-th atoms is determined by the gradient with respect to atomic displacement as **Equation 7**.

$$F_i = -\nabla_{r_i} U(r_1. \ldots . r_N) = -\left(\frac{\partial U}{\partial x_i}. \frac{\partial U}{\partial y_i}. \frac{\partial U}{\partial z_i}\right) \quad (7)$$

Regarding the development of force field, the ability for bond breaking and new bond formation without simulating the electrons themselves have been proposed by researches. For example, TTAM,[42] BKS[43] and Tersoff[44-46] in which the charge of the coulomb interactions is fixed. These available potentials are less reliable in the systems by means of MD simulation that need charge adjustment in response to changing system conditions. The reactive force field (ReaxFF) is suggested.[47] This force field can describe charge transfer scheme however, it cannot cover the full range of bonding types operating in a wide range of systems. Recently, a more robust and flexible reactive force field (COMB)[4] is developed in which atomic charges are allowed to change dynamically with the changing system condition and can capture the effect of the full range of bonding types.

The Al_2O_3 NP has been generated with the radius given in **Tables 4**. The dimension cell is calculated according to the NP size and the volume fraction of 1%. The NP has been constructed with 650 Aluminum and oxygen atoms while different number of CO_2 molecules has been initially applied at different SC conditions based on the experimental value of pure CO_2 density at the given temperature and pressure. **Table 4** shows the basic case at temperature 380 K and pressure 200 bar. According to reference,[48] density of pure CO_2 is considered 0.46 gr/cm^3 for different size of nanoparticles as BCase#1, BCase#2, and BCase#3.

Table 4: Initial parameters for liquid SC- CO_2 at P=200 bar and T=380 K

	Nanoparticle Al_2O_3	Box

Based Case	Vol. Fraction 1%		Nanoparticle Radius	Nanoparticle Volume	Lattice Volume	Lattice length
ρ_{CO_2}	0.46 (gr/cm^3)[48]		r (nm)	V_{NP} (nm^3)	V_t (nm^3)	a(nm)
BCase#1	d_1 (nm)	1.000	0.500	0.524	52.360	3.741
BCase#2	d_2 (nm)	1.250	0.625	1.023	102.265	4.676
BCase#3	d_3 (nm)	1.500	0.750	1.767	176.715	5.612

In this study, the interaction parameters between the Al_2O_3 NP and CO_2 molecules have been modeled using COMB potential[4] that include both charge transfer and the many-body interactions and can provide a flexibility for modeling the systems including the full range of bonding types. There is one spherical Al_2O_3 NP in the systems including CO_2 molecules (**Figure 1**) at different temperatures as given in **Tables 5** and **6**. Atomic structures for MD calculations have been visualized using OVITO.[55]

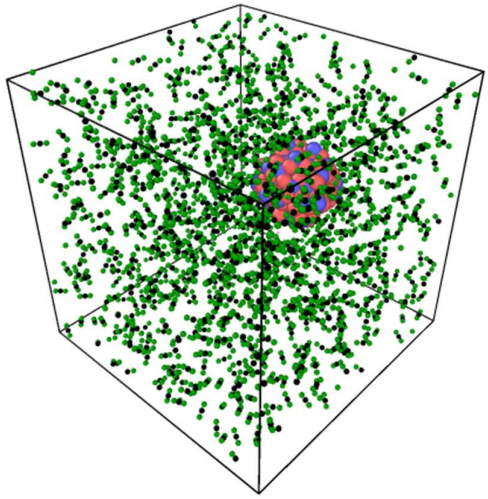

Figure 1: Sample of Volume control for Al_2O_3 NP in SC- CO_2 liquid at the first step of modeling before applying pressure and temperature, Color scheme, liquid SC- CO_2 (O=Green, C=dark brown), Al_2O_3 NP in liquid SC-CO2 (Al=red, O=Blue)

Tables 5 and **6** show temperature at 350 K and 410 K respectively, where the density of CO_2 depends on temperature and decreases by increasing temperature. The system tabulates at two

temperatures 350 K and 410 K are named Lower Based Case and Upper Based Case, respectively.

Table 5: Initial parameters for liquid SC- CO_2 at P=200 bar and T=350 K

Lower Based Case	Nanoparticle Al_2O_3				Box	
	Vol. Fraction 1%		Nanoparticle Radius	Nanoparticle Volume	Lattice Volume	Lattice length
ρ_{CO_2}	0.61 (gr/cm^3)[48]		r (nm)	V_{NP} (nm^3)	V_t (nm^3)	a(nm)
LCase#1	d_1 (nm)	1.000	0.500	0.524	52.360	3.741

Table 6: Initial parameters for liquid SC- CO_2 at P=200 bar and T=410 K

Upper Based Case	Nanoparticle Al_2O_3				Box	
	Vol. Fraction 1%		Nanoparticle Radius	Nanoparticle Volume	Lattice Volume	Lattice length
ρ_{CO_2}	0.35 (gr/cm^3)[48]		r (nm)	V_{NP} (nm^3)	V_t (nm^3)	a(nm)
UCase#1	d_1 (nm)	1.000	0.500	0.524	52.360	3.741

In all cases, first, the system has been pre-equilibrated for 200 ps at the desired temperature by carrying out the isothermal NVT canonical ensemble for the system of atoms which initially arranged in a perfect structure lattice. Second, the isothermal-isobaric NPT ensemble has been carried out at the desired temperature and pressure. This ensemble has been applied for 500 ps, for the system including the Al_2O_3 NP in order to reach the equilibrium thermodynamic state. Then, the average densities and thermo-physical properties (i.e., viscosity and diffusion) of the systems are calculated by averaging over 400 ps trajectory. The methods used to calculate viscosity and diffusion has been explained below.

Figure 2 shows the final step of modeling the system including Al_2O_3 NP and CO_2. The distribution of atoms has been changed in the volume due to apply pressure. As it mentioned before, the boundary condition is periodic and so the volume has been changed to set pressure

in NPT ensemble. This ensemble takes the most time of the ensembles because of preventing agglomeration in the system. This figure shows the adsorption of the CO_2 molecules by the Al_2O_3 NP at the end of the simulation for the Based Case.

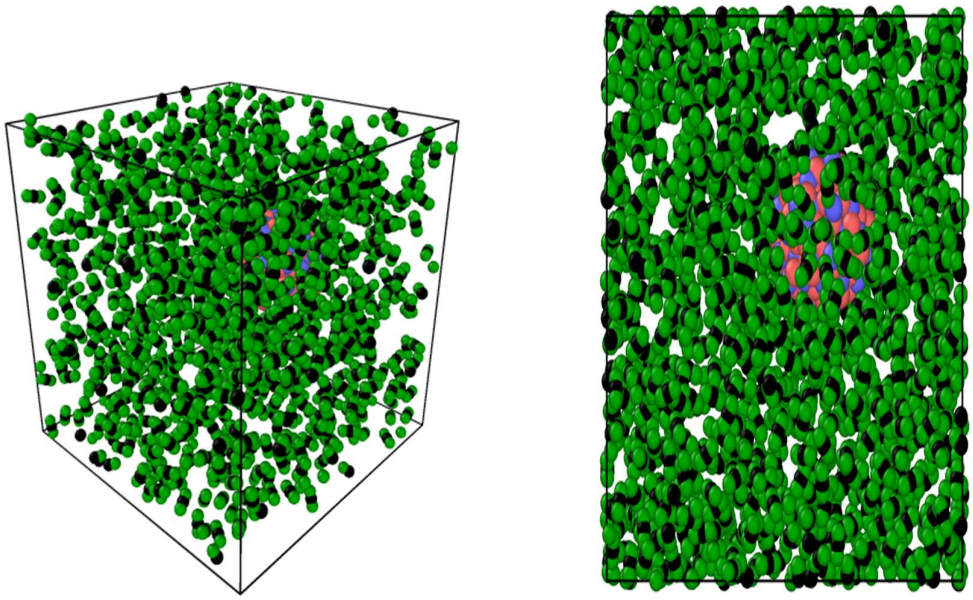

Figure 2: Sample of volume control for Al_2O_3 NP in SC- CO_2 liquid at the final step of modeling after applying pressure and temperature

3.1 Viscosity

MD simulation can calculate viscosity using different methods. In this study, the method of calculation follows Green-Kubos (GK) formula[49] which is one of the methods used in LAMMPS's calculation. So, the formula involves η as shear viscosity which it can be related to the correlation functions of the corresponding tensor in thermal equilibrium. The shear viscosity η of a fluid is evaluated in the following **Equation 8**:

$$\eta = \frac{V}{K_B T}\int_0^{\infty} \langle \sum_{x<y} P_{xy}(t) P_{xy}(0) \rangle \, dt \qquad (8)$$

Where V is the volume of the system, T is the temperature, K_B is Boltzmann's constant, and P_{xy} refers to an independent component of the stress in the xy direction. The brackets <. . .> denote an average over an equilibrium ensemble.

In GK formula, the stress autocorrelation function (SAFC) is calculated as follows:

$$C_\eta(t) = \langle \sum_{x<y} P_{xy}(t) P_{xy}(0) \rangle \quad (9)$$

Equation 9 uses a single summation that allows all atoms have been consolidated into a single autocorrelation function. This method of calculation is used to simulate in MD whereas alternative formulation based on particles displacement require translational invariance which utilizes periodic boundary conditions.

3.2 Diffusion Coefficient

The diffusion coefficient of the system is calculated by the mean-squared displacement (MSD). This diffusion coefficient, D, is measured to investigate the effect of diffusion rate within the system. The diffusion coefficient is measured using the Einstein relation[38] as follows:

$$D = \frac{1}{6} \lim_{t \to \infty} \frac{d}{dt} \langle (r_i(t) - r_i(0))^2 \rangle \quad (10)$$

Where $r_i(t)$ is the position of the center of mass of the molecules i at time t, $r_i(0)$ is the initial position, and $<(r_i(t) - r_i(0))2>$ indicates an ensemble average which is MSD. According to **Equation 10**, the slope of the MSD is proportional to the diffusion coefficient of the diffusing atoms in the canonical ensemble. So, by taking the slope of the trajectories of the line of calculated MSD over the averaging period, the diffusion coefficient is calculated. The calculated MSD as a function of time for the Based Case are shown in **Figure 3**. The results indicate that MSD has a direct relationship with NP size.

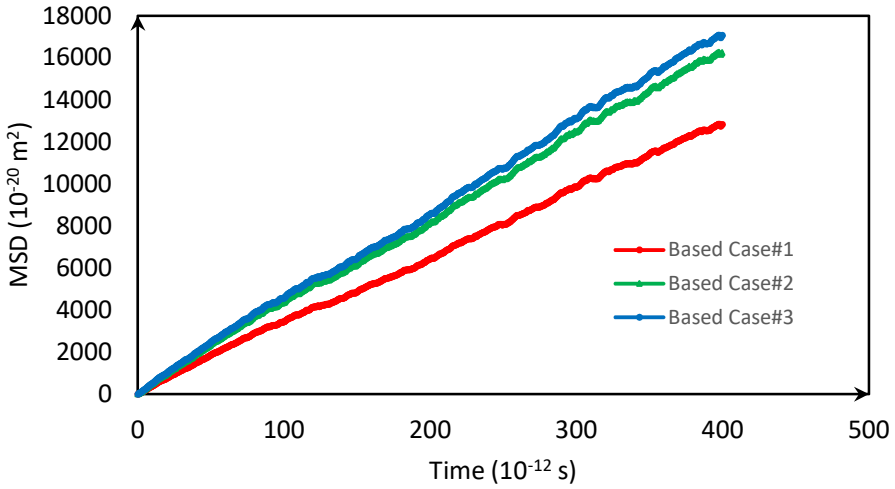

Figure3: MSD via time for Based Case#1-3, effect of NP size

As explained by khaledialidusti et al.[24], the system-size could affect the accurate calculation of the diffusion coefficient; however, in this system, the system-size is large enough to calculate the accurate value of the self-diffusion coefficient.

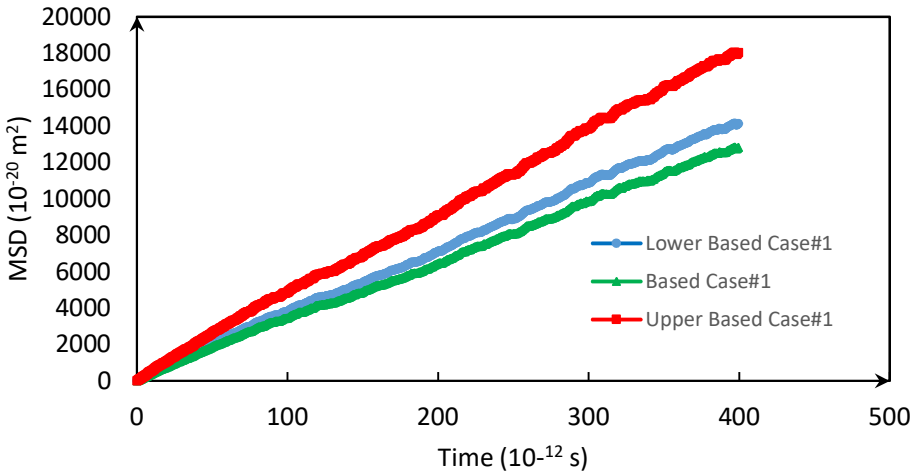

Figure4: MSD via time for Based Case#1-3, effect of temperature

Figure 4 indicates the temperature effect on MSD and illustrates that temperature has direct relationship with MSD value. Later, this will be discussed how highly diffusion coefficient has effect changes.

4. Result and Discussion

In technological applications, metal oxide NPs have been widely developed to make special properties as nanofluids with respect to those of bulk for employing in different industry such as oil and gas. The metal oxide NPs exhibit unique chemical and physical properties due to their high density and limited size of corner or edge on the surface sites. Currently, several types of metal oxides nanoparticles play a very important role in numerous areas of petroleum such as CuO and Al_2O_3. Due to high efficiency of these nanoparticles to improve the thermosphysical properties of fluids, researchers have done special study on these NPs. So, they have evaluated the efficiency of these NPs on the rheological properties of the nanofluid in the petroleum industry wherein the higher pressures and temperatures in oil wells pose significant challenges for improving oil and gas production.

High temperature and pressure mainly affect the thermophysical properties such as viscosity and self-diffusion coefficient of SC-CO_2. NPs may overcome this challenge by improving the viscosity of the degraded liquid. In our previously published study,[24] we showed the enhancement of rheological properties of SC-CO_2 using metal oxide CuO NPs to inject in oil reservoir at relevant temperature from 380 K to 410 K and pressure from 200 bar to 350 bar. So, we evaluated that the viscosity of the SC-CO_2 could increase up to 2.5 times by adding CuO NP. R. Khaledialidusti et al[24] suggested modeling of pure SC-CO_2 by COMPASS potential in MD simulation has excellent agreement with experimental results.[50] Also, they proposed the self-diffusion coefficient of MD can follow the trend of the experimental results for SC-CO_2 are obtained (see Figure 15[24]).

This study has suggested other metal oxide NP like Al_2O_3 to compare the enhancement of the thermophysical properties of SC- CO_2 with the previous result.[24] So, this study has modeled NP in spherical shape and investigated the effect of four major parameters such as Al_2O_3 NP size, temperature, NP spherical shape, and NP-based material on the viscosity and the self-

diffusion coefficient of SC-CO_2. The novelty of this study is related to using Al_2O_3 in SC-CO_2 and comparing effect of two metal oxides on the viscosity and evaluating the size effect of NPs in SC- CO_2.

4.1 Effect of NP size and temperature on the viscosity of the nanofluid

In this section, firstly, the effect of NP size on the relative viscosity and diffusion coefficient is evaluated in three cases at constant pressure, 200 bar, and temperature, 380 K, as the Based Case. Secondly, temperature is changed and its influence on the normalized viscosity is discussed. **Figure 5** illustrates the relative viscosity and diffusion of Al_2O_3-CO_2 system to the reference SC-CO_2 system. The results suggest that the fluid properties are greatly enhanced by adding of NPs. It is also found that Al_2O_3-CO_2 system has lower diffusion rate and higher viscosity rate at smaller NP size. It is shown that enhancement of viscosity rate is decreased at larger NP size and the diffusion rate is also less increase at larger NP size. Gerardi et al.[51] proposed a decay trend in the diffusion coefficient to describe this event.

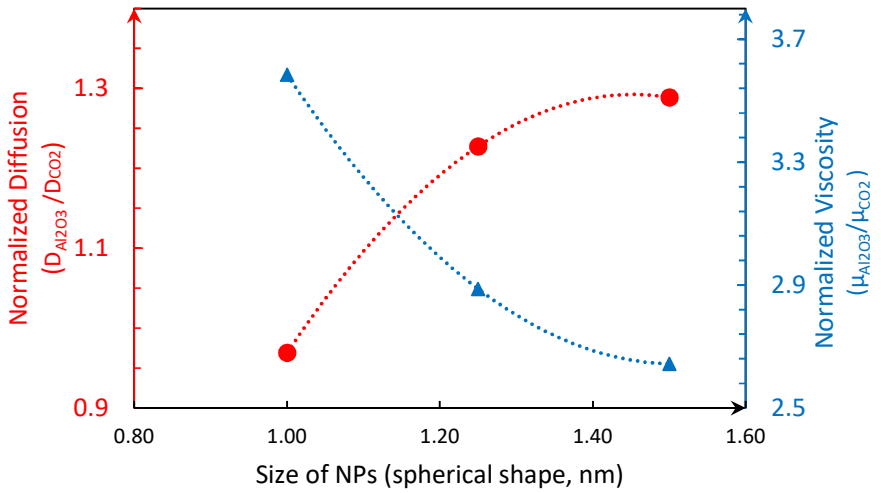

Figure 5: Normalized self-diffusion coefficient and normalized viscosity of Al_2O_3 NP SC-CO_2 nanofluide for Based Case at different particle size (spherical shape, diameter, d=1, 1.25, and 1.5 nm)

In order to evaluate direct relationship between the normalized self-coefficient changes and the size of Al_2O_3 NP, F. Ould-Kaddour et al.[52] suggested a detail description of the diffusion

process. So, it needs to go through how this process varies with the NP size in the based fluid by the computation of the velocity autocorrelation function (VAF). It implements that the NP size has an opposite relationship with VAF. So, because the diffusion phenomena is happening in Newtonian fluid, this coefficient of small spherical particle in constant temperature, 380 K, is inversely proportional to the particle size and the viscosity of SC- CO_2.

Figure 6 shows the variation of the relative viscosity with temperature for constant pressure 200 bar. As it is shown the relative viscosity is proportional to temperature and this relationship is more effective in higher temperature. As this figure indicates, the normalized viscosity for 350 K and 410 K is 1.94 and 3.68, respectively. It is drastically increased and make the researchers encouraged to use Al_2O_3 NP to enhance viscosity of a based liquid at high temperature.

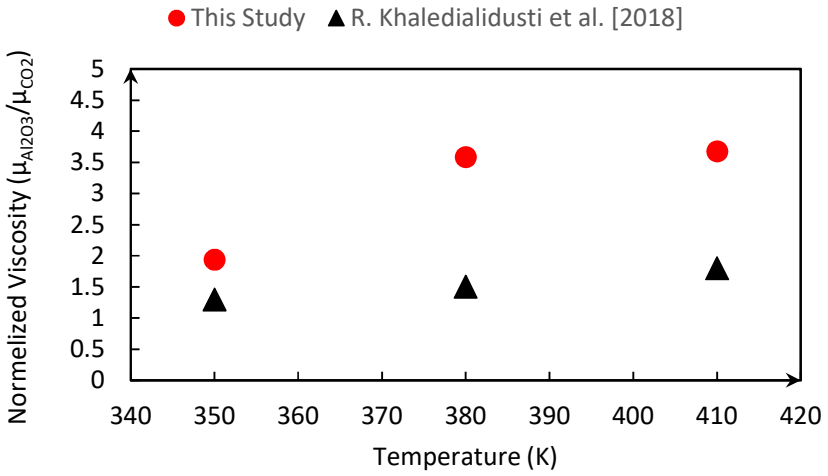

Figure 6: Normalized viscosity for pressure 200 bar at different temperature (BCase#1, LCase#1, UCase#1)

As it can be seen, the temperature effect on the diffusion coefficient is shown in **Figure 7**. This nanofluid follows Newtonian fluid's behavior and clearly self-diffusion coefficient, the normalized self-diffusion coefficient describes the ability of a CO_2 molecule movement among the other molecules in the system, has opposite relationship to temperature and this is

confirmed that the NP could attract CO_2 molecules around itself and prevent them to diffuse into each other. In fact, the results of the relative viscosity and self-diffusion coefficient suggest that the fluid properties are greater enhanced with temperature by the Al_2O_3 NP. In the next section, effect of material types and shapes of NPs will be discussed for aluminum oxide and copper oxide NP.

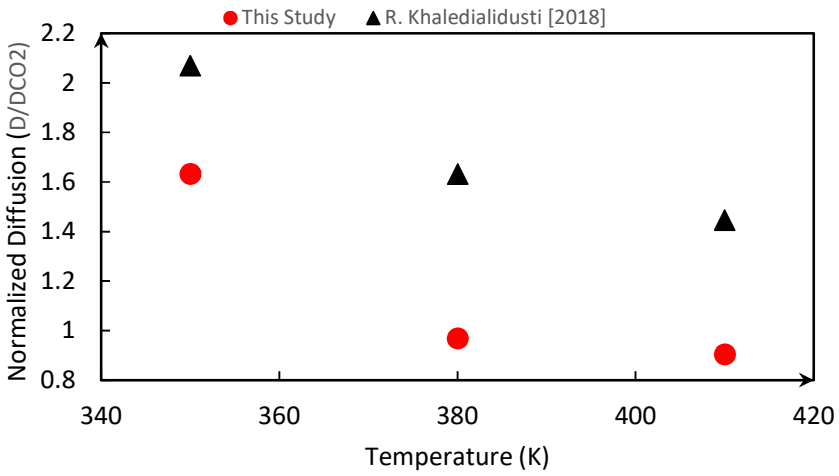

Figure 7: effect of temperature on normalized diffusion coefficient for Based Case#1

4.2 Effect of particle shape and material types on the viscosity of the nanofluid

Different categories of nanoparticles with different shapes and material types depending on the application can be applied in the fluid. The most popular material type used oxides and carbon based materials as NPs. There are many studies to implement Al_2O_3 NPs in nanofluids such as ethylene glycol[53], PG (propylene-glycol)[54], EG(propylene glycol)[55], Glycerol-watre[56], and Water[57-62] because Al_2O_3 may effectively enhance rheological properties of the based fluids and has low cost in spherical NPs shape.

This study deals with increasing viscosity of SC-CO_2 for employing as EOR so, the metal oxide type Al_2O_3 is more suitable nanoparticles to be added to SC-CO_2 as a based fluid to provide the fluid a better viscosity. Regarding the literatures, the most studies focused on water and

none of them consist of CO_2 or SC- CO_2 as a based fluid. Furthermore, they considered spherical shape in most cases because there is no need to find the greatest energy surface as the authors applied DFT to find that[24] and spherical shape is more practical to use in the industry.

After discussing the reasons of choosing the NP shape and the material type, we investigate the effects of these two parameters on the viscosity of SC-CO_2 by comparing with our previous study[24]. So, there are two NP shapes which constructs two metal oxides material type, one of them is Al_2O_3 NP with spherical shape and the other one is CuO NP with cylindrical shape. Later, it will be comparatively shown and discussed how significantly these two NP types can enhance the relative viscosity and self-diffusion coefficient of SC-CO_2 nanofluids and then come to conclusion which types may be better choice to improve them.

Figures 6 and **7** indicate the results of the simulation Al_2O_3 NP SC-CO_2 nanofluid system for self-diffusion coefficient and relative viscosity as a function of NP size, respectively, and also compare martial type effect on the properties.

Figure 6 shows the variation of the relative viscosity via NP size for Based Case and indicates the opposite relationship with NP size. At the smaller NP size, it has greater impact on the enhancement of the viscosity of the reference CO_2. Furthermore, we clearly observe that Al_2O_3 NP is more effective to enhance the viscosity of SC-CO_2 in comparison with CuO NP. For example, for 0.5 nm Al_2O_3 NP size, the relative viscosity of the nanofluid is increased from 1.936 to 3.584 and then to 3.676 for temperature increasing from 350 K to 380 and then 410 K. Similar behavior is also found for equivalent radius 1.144 nm of CuO NP size, the relative viscosity is increased from 1.298 to 1.502 and then to 1.799 for the same temperature range mentioned above. It is interesting to observe that the viscosity of nanofluid with 0.5 nm Al_2O_3 particle size is clearly greater than 1.144 nm CuO particle size. Although, the equivalent radius of CuO NP is almost 1.26 bigger than the smallest radius of Al_2O_3 NP; however, Al_2O_3 NP can increase the relative viscosity of the nanofluid more significantly than CuO NP where the

differences is considerable and it is about 1.56 times viscosity enhancement of CuO NP. It definitely can be related to the NP based-material.

It can be concluded that the temperature and material type of NP are crucial parameters that have to be considered simultaneously to have the best choice of NP for this application. General conclusion is that the viscosity enhancement of Al_2O_3 NP is more effective than CuO NP. To more accurate compare of the cylindrical CuO NP to the two shapes of NP, it is essential to consider the equivalent radius have a comparable parameter so, **Figure 8** shows bar diagram to compare the percentage of enhancement for the two types of NP.

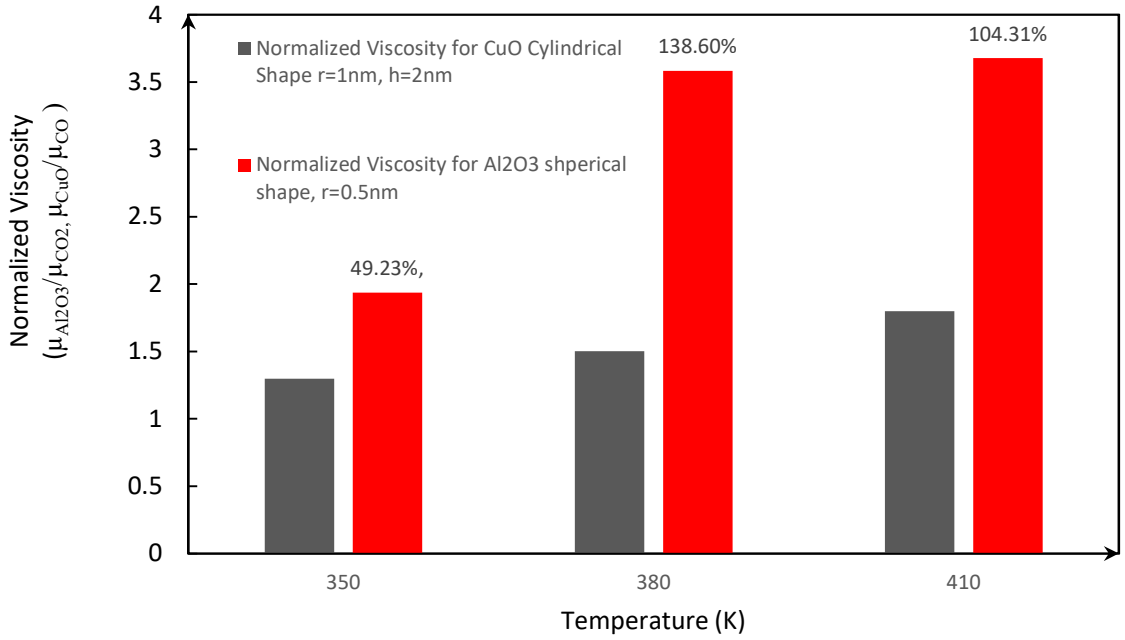

Figure 8: Comparing effects of Al_2O_3 NP with CuO NP on relative viscosity of SC- CO_2

Figure 8 illustrates that the enhancement of the relative viscosity using the spherical shape Al_2O_3 NP is more considerable than the CuO NP. In spite of the fact, Al_2O_3 NP is smaller than CuO NP, Al_2O_3 NP improves greatly in relative NP volume to the normalized viscosity, especially in higher temperature.

5. Summary and Conclusion

Thermophysical properties of the SC-CO_2 applying a recovery liquid in oil reservoirs are studied in this literature. CO_2 injection method is not robust in high temperature and pressure conditions due to low viscosity. So, one solution is using nanoparticles to enhance thermosphysical properties of the liquid in harsh conditions. To the best knowledge of the authors, literatures have never focused on calculating the rheological properties of SC-CO_2 using molecular dynamic (MD). In our previous published study, we evaluated the viscosity enhancement of the SC-CO_2 by using metal oxide CuO NPs. We indicated that adding NPs in SC-CO_2 enhance the viscosity of the liquid approximately 1.3 to 2.5 times This study proposes modeling of Al_2O_3 NP-SC- CO_2 nanofluid by using two COMPASS and COMB force fields which were already validated by experimental results. Four major parameters have been evaluated such as effect of Al_2O_3 NP size, temperature, shape of the nanoparticles, and material types on the viscosity and the self-diffusion coefficient of SC-CO_2.

The novelty of this study is using Al_2O_3 in SC-CO_2 and comparing the effect of two metal oxides on the viscosity and evaluating size effect of NPs in SC-CO_2. In this study, in the first step, effects of NP size are evaluated for three different NP size at constant pressure, 200 bar, and temperature, 380 K, on the relative viscosity and self-diffusion coefficient. The relative viscosity is enhanced almost 3.67 times for smallest NP, radius 0.5 nm. In addition, it is illustrated normalized diffusion coefficient has direct relationship with NP size. Moreover, this study evaluates the effect of temperature on the normalized viscosity at the constant pressure, 200 bar, and different temperatures changing from 350 K to 410 K. The results show that this property has an opposite relationship with the NP size.

In the next step, this study also compares two base-material types of NPs, one of them is Al_2O_3 NP with spherical shape and the other one is CuO with cylindrical shape. Consequently, the results show that Al_2O_3 NP has a greater impact on the enhancement of the viscosity of the reference CO_2 at the same size of the NP. For example, the smallest Al_2O_3 NP increase the

relative viscosity from 1.93 to 3.67 for temperature increasing from 350 K to 410 K. In addition, similar trend is also found for CuO NP, the relative viscosity was enhanced from 1.29 to 1.79 for the same temperature ranges mentioned. It is interesting to observe that the viscosity of Al_2O_3 –SC-CO_2 nanofluid is clearly greater than CuO SC-CO_2 nanofluid. Such differences become more pronounced for temperature 380 K. It may be concluded that the temperature and material type are crucial parameters have to be considered simultaneously to have the best choice of NP for this application. Also, the self-diffusion coefficient of MD has been studied and shown that it follows the opposite trend of the viscosity due to Newtonian fluid's behavior of the nanofluid, in temperature from 350 K to 410 K at 200 bar pressure.

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