



Research Article

Molecular dynamics simulation of water–graphene nanofluid

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Abstract

Our goal in this work was to study the effect of graphene nano-sheets' size on the graphene/water nanofluid viscosity using molecular dynamics simulation. Prior to the calculation of the viscosity of the nanofluid, a validation of the computational strategy and the simulation model was tested and the results of the viscosity and density of water molecules with SPC/E, TIP3P and TIP4P potentials at 298 K were compared to the experimental data. It was found that the TIP3P potential gives better result for the viscosity, hence was used in our further calculations. Simulations were conducted at room temperature (298 K) and atmospheric pressure with the Berendsen algorithm. The system was initially run for 300 ps under the NVT conditions. Finally, the production steps of 2 ns with the integral step of 1 fs were performed. Two graphene sheets of the sizes of 20×20 and 10×10 nm² were considered. It was observed that the viscosity of nanofluids containing smaller particles is higher than that of the nanofluids containing higher-diameter particles. Moreover, to obtain a better insight into the local structure and organization of the studied system, the site–site and center of mass radial distribution functions (RDFs) were studied. RDFs of oxygen and hydrogen atoms of water molecules were calculated. The obtained RDFs showed that distinct layers of water molecules are formed near the graphene sheet. The observed peaks in the RDF graphs show strong interactions between water molecules and graphene sheet.

Keywords Nanofluid · Dynamic viscosity · Molecular dynamics simulations · Radial distribution function · Potential functions · Graphene · Carbon nanostructures

1 Introduction

Heat transfer systems need improvement in performance to become more energy efficient. Many industries need ultra-high performance in cooling and heating. Thermal management of electronic components has attracted a lot of attention due to the drastic increase in power density, compactness and enhancement in computation speeds which lead to high heat fluxes [1, 2]. But the existing techniques are not adequate to satisfy the thermal management requirements of the high-power density devices. A fluid with improved heat transfer properties can solve this issue. The thermal and heat transfer properties of the conventional cooling fluids are enhanced by suspending nanoscale-sized (1–100 nm) solid particles with higher

thermal conductivity and high surface area [3]. Nowadays, nanofluids because of their improved thermal properties [4–6] are extensively used in a wide variety of applications, such as industrial and electronic cooling, lubrication, comfort air conditioning and extraction of geothermal and solar energy. There are only a few recent studies on thermo physical properties and surface tension of nanofluids in the literatures. In recent years, the family of carbon forms has attracted considerable attention with the discovery of the other carbon structures such as fullerenes and carbon nanotubes. In the graphene sheets, carbon atoms are joined by covalent bonds and located in a honeycomb lattice. The graphene properties are interesting among other carbon configurations. Thus, our goal in this section is to study the effect of the size of graphene nanoparticles on

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the viscosity of water–graphene nanofluid using MD simulation. We also investigate how nanoparticles alter the viscosity of nanofluids from microscopic point of view.

1.1 Water potential

Water and aqueous solutions are principle subjects in computational chemistry. Water models are used to simulate and calculate the thermodynamic properties of water clusters, liquid water, and aqueous solutions. Many types of these models are derived from quantum mechanics, classic mechanics, experimental results, and the combination of them. In general, water models can be classified by following three points; (i) the number of interaction points called *site* (ii) rigidity or flexibility of the model (Rigid and Flexible models) (iii) whether the model includes polarization effects (Polarizable models). Rigid water models are considered as the simplest water models. The bond lengths, including a fictitious H–H bond, are constrained using the SHAKE algorithm and bonding interactions are treated by holonomic constraints. On the other hand, the flexible models include bond stretching and angle bending as well as all degrees of freedom for the OH bonds and HOH bond angle. Flexible models can reproduce vibration spectra with agreeable results. Polarizable water models contain an explicit polarization term, which is essential to simulate water in different phases with acceptable results. All water molecules potentials used here were composed of Lennard-Jones (LJ) and Coulombic terms. Lennard-Jones term simulated the dispersion and repulsion forces and the electrostatic interactions were modeled by Coulomb's law. The overall form is represented as follows:

$$E_{ab} = \sum_i \sum_j \frac{kq_i q_j}{r_{ij}} + \frac{A}{r^6} - \frac{B}{r^{12}} \quad (1)$$

where k_C is the electrostatic constant with the magnitude of $332.1 \text{ \AA kcal}/(\text{mol } e^2)$ with the units commonly used in molecular modeling; q_i and q_j are the partial charges relative to the charge of the electron; r_{ij} is the distance between two atoms or charged sites; and A and B are the Lennard-Jones parameters. In these models the point charge may be located on the atoms or on dummy sites and the interactions between oxygen atoms are considered by Lennard-Jones parameters. Figure 1 shows the general shape of the 3- to 6-site water models. These water models are similar in nature but the exact geometric parameters, the OH bond length and the HOH angle, differ between them which lead to substantial differences in calculated liquid water properties.

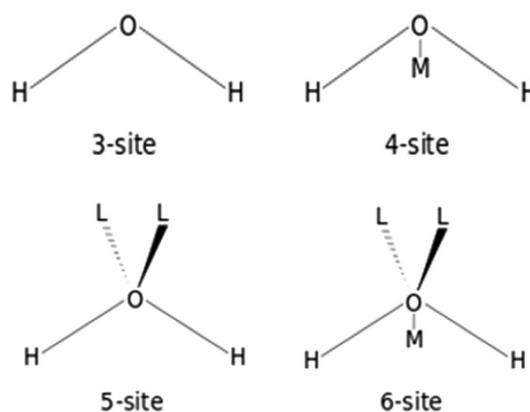


Fig. 1 The general shape of the 3- to 6-site water models

Table 1 The parameters for some potential models

| | TIP4P | SPC | TIP3P | SPC/E ^a |
|---|--------|--------|--------|--------------------|
| $r(\text{OH})$ [Å] | 0.9572 | 1.0 | 0.9572 | 1.0 |
| HOH [°] | 104.52 | 109.47 | 104.52 | 109.47 |
| A [$10^3 \text{ kcal } \text{Å}^{12}/\text{mol}$] | 600.0 | 629.4 | 582.0 | 629.4 |
| B [$\text{kcal } \text{Å}^6/\text{mol}$] | 610.0 | 625.5 | 595.0 | 625.5 |
| $q(\text{O})$ | −1.04 | −0.82 | −0.834 | −0.8476 |
| $q(\text{H})$ | +0.52 | +0.41 | +0.417 | +0.4238 |

^aThe SPC/E model adds an average polarization correction to the potential energy function

Two-site models of water have two interaction points and are used mostly to calculate the dielectric properties of water by means of site-renormalized molecular fluid theory. In Three-site models there are three interaction points corresponding to the three atoms of the water molecule, and the site corresponding to the oxygen atom also has the Lennard-Jones parameters. Because of the high computational efficiency and simplicity, 3-sites water model is widely used in molecular dynamics simulations. Table 1 lists the parameters for some potential models.

The four-site model has four interaction points: three atoms of the water molecule and one dummy atom with negative charge close to oxygen (along the bisector of the HOH angle of the three-site models). OH distance and HOH angle, in most four-site water models, are identical to that of the free water. The newer models are parameterized by Metropolis Monte Carlo or molecular dynamics simulations which have improved the electrostatic distribution around the water molecule.

Table 2 Computed density and viscosity of water at selected temperature

| | SPC/E | TIP3P | TIP4P | EXP |
|-------------------------------|---------|---------|---------|---------|
| Density (gr/cm ³) | 1.04 | 0.99 | 1.02 | 1 |
| Viscosity (Pa s) | 0.00031 | 0.00071 | 0.00063 | 0.00085 |

2 Graphene model

For the graphene sheet we used a combination of L-J12-6 potential and Coulomb potential

$$U(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{r_{ij}} \quad (2)$$

where r_{ij} is the distance between atoms i and j , q is the partial charge assigned to atom i , σ_{ij} and ϵ_{ij} are energy and size parameters. The interaction between graphene sheet and water molecules was considered by Lorentz-Berthelot combining rules,

$$\sigma_{ij} = (\sigma_i + \sigma_j) / 2 \quad (3)$$

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad (4)$$

2.1 Water density and viscosity

Prior to the calculation the viscosity of nanofluid, validation of the computational strategy and the simulation model was investigated. All molecular dynamics simulations were performed using the LAMMPS¹ (Large-scale Atomic/Molecular Massively Parallel Simulator) open-source molecular Simulation package. A cubic box with periodic boundary conditions in all three directions was used contained water molecules. Simulations were performed in the NVT ensemble. The system was initially run for 300 ps under the NVT condition. Finally, the production steps of 1 ns with the integral step of 1 fs were performed.

In Table 2, the results of the viscosity and density of the water molecules with SPC/E, TIP3P and TIP4P potentials at 298 K are represented. Experimental results are also reported for comparison. TIP3P potential has given better result for viscosity. For the next calculations we will use TIP4P potential.

A cubic box with periodic boundary conditions in all three directions was used ($3.7 \times 3.7 \times 3.9$ nm). The simulation box consists of liquid water and graphene with 1×1 nm in length. Water atoms were initially distributed homogeneously in the box and graphene sheet was placed in the middle of the box, along the z -axis. Our

simulation box, composed of water molecules and one graphene sheet. The simulated graphene surface is non-polarisable [7] and the graphene sheets were frozen during the simulation.

Simulations were performed in the NVT ensemble. Long-range electrostatic interactions were handled using the Particle-Particle Particle-Mesh K-space (PPPM) solver [8]. The cut-off distance was set to 10 Å, for short-range van der Waals forces. Simulations were conducted at room temperature 298 K and atmospheric pressure with the Berendsen algorithm [9]. The system was initially run for 300 ps under NVT condition. Finally, the production steps of 2 ns with the integral step of 1 fs were performed. Figure 2 shows the simulation box before and after the equilibrium calculations.

Two graphene sheets with 20×20 and 10×10 nm lengths (Fig. 3) were considered in the simulations in order to study the effect of the nanoparticle size on the viscosity of nanofluids.

We used Green-Kubo (GK) method to study the viscosity. The GK method is a well-established technique that is widely used for determining the nano fluids viscosity. In this method, transport coefficients are estimated with the integral of an accurate time-correlation of the equilibrium fluctuations of the corresponding flux via the fluctuation-dissipation theorem and linear response theory [10]. The shear viscosity is computed according to the following equation

$$\eta = \frac{V}{3k_B T} \int_0^\infty \langle P_{xy}(0) P_{xy}(t) \rangle dt \quad (5)$$

where η , V , T and k_B are the shear viscosity, the volume of the system, the temperature and Boltzmann's constant respectively. P_{xy} is pressure (stress) component in the xy direction [11]. The integrand is the autocorrelation function of the pressure tensor P .

The results of the computed viscosity (Pa s) of graphene-water systems are summarized in Table 3. The results show that all the graphene/water nanofluids have higher viscosity compared to pure water in all cases. It is also observed that the viscosity of the nanofluids changes reversely with increase in the diameter of nanoparticles dispersed in the base fluid. Therefore, at a constant temperature, the viscosity decreases with the increment of graphene sheet size. The results are in well agreement with the experimental reports, which indicate decrease in the viscosity of graphene/water nanofluid with increase in the nanoparticles size [12]. These trends are mainly the result of strong interactions between graphene and water molecules and consequently stronger water-water interactions. It can be also due to the hydrogen bonds. In general, a larger amount of the hydrogen bonds

¹ <https://lammps.sandia.gov/>.

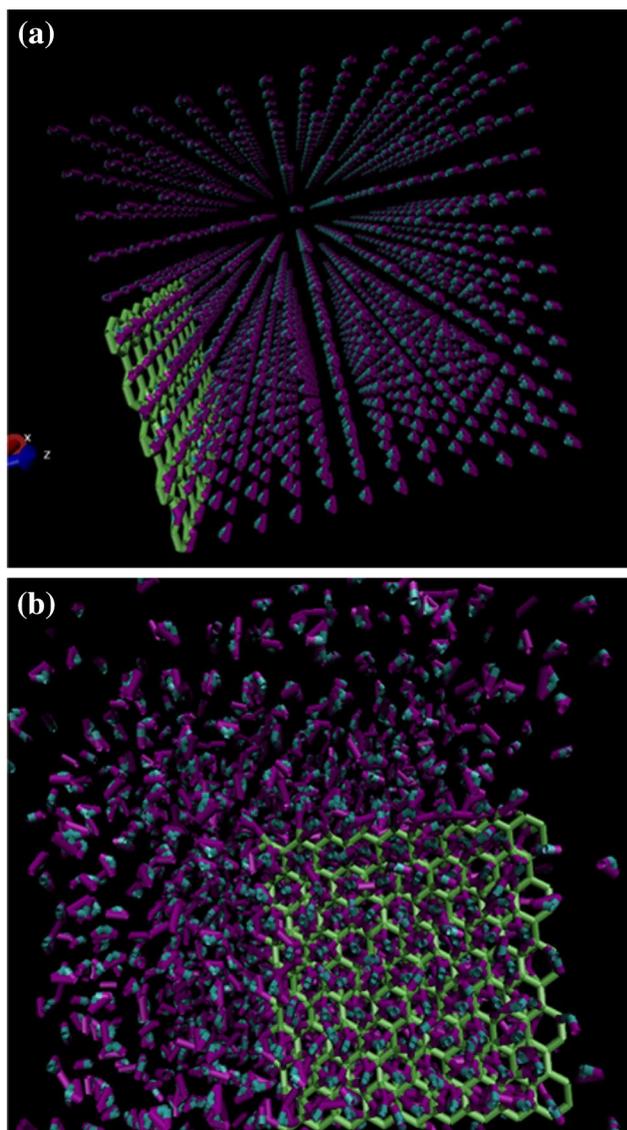


Fig. 2 Initial (a) and final structure (b) of molecular dynamic model of graphene/water with periodic boundary conditions in 3 directions

implies stronger intermolecular interactions among the molecules, which can lead to an increase in the viscosity.

2.2 The self-diffusion coefficient

The self-diffusion coefficient (D) can be calculated from the Green–Kubo formula and from the Einstein correlation. The most common method applied for calculating self-diffusion coefficient, is the Einstein correlation. The Einstein correlation is as follows

$$D = \frac{K_B T}{6\pi r \eta} \tag{6}$$

where η is the viscosity and r is the radius of the spherical particle. Indeed, the diffusion coefficients can be computed from the mean squared displacement (MSD) plots in case a diffusive regime can be established at relatively long simulation times. Mean squared displacement (MSD, also mean square displacement, average squared displacement, or mean square fluctuation) is a criteria of the deviation of a particle from a reference position over time. It is the most common measurement of the spatial extent of random motion which can be considered as measuring the portion of the system “explored” by the random walker as well. In the realm of biophysics and environmental engineering, the Mean Squared Displacement is measured over a time interval to determine if a particle is spreading solely due to diffusion. The MSD is defined as

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle |r_i(t) - r_i(0)|^2 \right\rangle \tag{7}$$

where $r_i(t)$ is the position of the center of mass of the molecule at time t . The slope of the MSD as a function of time could be used to estimate the self-diffusion coefficient for water molecules in the direction parallel to the surface. Each simulated MSD for the graphene/water systems were performed for 2 ns. We estimated self-diffusion coefficient by plotting MSD as a function of time.

The plot of $\log(\text{MSD})$ versus $\log(t)$ is also utilized to ensure that the simulation has been long enough and the diffusive regime has been reached.

$$\beta = \frac{d \log(\text{MSD})}{dt \log(t)} \tag{8}$$

In the physical diffusive regime, at very long times, the MSD of the ions increases linearly with time and β value is equal to one. For an accurate estimation of D , it is necessary for the liquid to be in a real diffusive regime. Accordingly, β values are obtained for water molecules from the log–log plot. The β plots of water are shown in Fig. 4.

The Magnitude of diffusion coefficient of interfacial water is estimated from the initial slope of the MSD data ($D = 2.5E - 9 \frac{m^2}{s}$). A direct comparison between the simulated self-diffusion coefficients and the experimental results show a relatively good coincidence between the simulated and experimental results [13].

2.3 Radial distribution function

The center of mass radial distribution functions (RDFs) which give the probability of finding a particle at a given distance were computed. RDFs give insight into the local structure and organization of the considered systems. In fact the RDF represents the variations of the density as a function of distance from a reference particle. Usually,

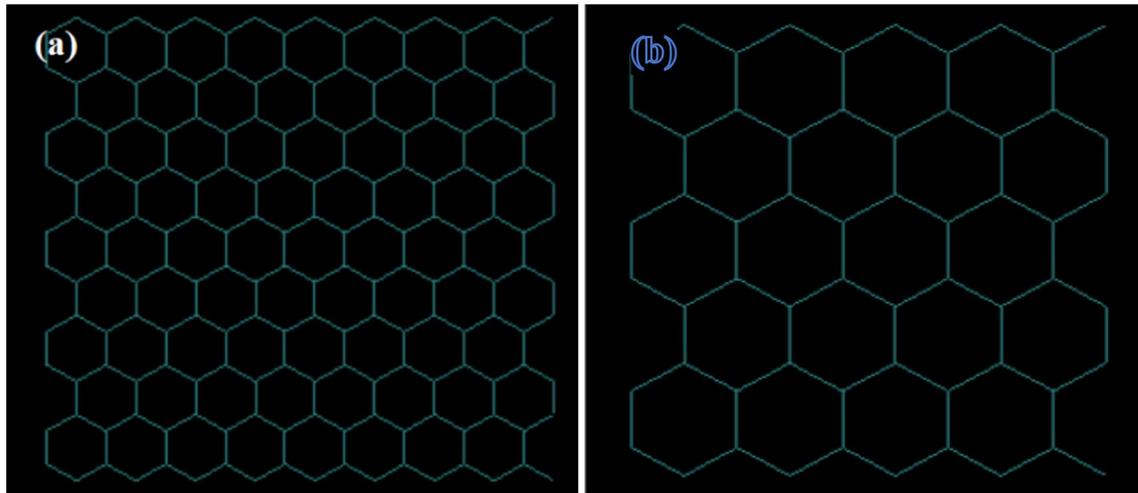


Fig. 3 Graphene sheets with 20×20 (a) and 10×10 nm length (b)

Table 3 The computed viscosity (Pa s) of graphene-water systems

| System | 10×10 | 20×20 | Bulk water ^a |
|-----------------|-------------|-------------|-------------------------|
| Viscosity(Pa.S) | 0.018±0.003 | 0.012±0.002 | 0.00085 |

^ahttps://www.thermexcel.com/english/tables/eau_atm.htm

RDF is used to analyze the phase state of particles in a system. Here, the RDFs of oxygen and hydrogen atoms of water molecules are calculated. Figure 5 shows the analysis of the site–site RDFs for the water molecules with the carbon atoms of the graphene. RDF plots show that distinct layers of water molecules are formed at the vicinity of graphene sheet. The peaks which are due to the interactions between water and the graphene molecules exhibit a strong interaction. In other words, the first peaks of the interactions between a water molecule and the carbons of graphene sheet are positioned at small distances. The obtained RDFs show that, 10×10 graphene sheet is more likely to form hydrogen bonds with the hydrogen atoms of water. A closer analysis of results shown in Fig. 5 show higher intensity and also a third peak at longer distances in the 10×10 graphene sheet, which indicate the stronger water interact with graphene sheet. Therefore, our calculations confirm that with the decrease of graphene sheet size viscosity increase. Decreasing the graphene sheet size caused less Brownian motion, smaller surface-to-volume ratio, and higher viscosity. It is worth mentioning that, particle size has a significant impact on the viscosity of nanofluids [14]. Some reported results show that with particle size reduction the viscosity increase [15]. On the other hand, completely opposite results have been reported [16].

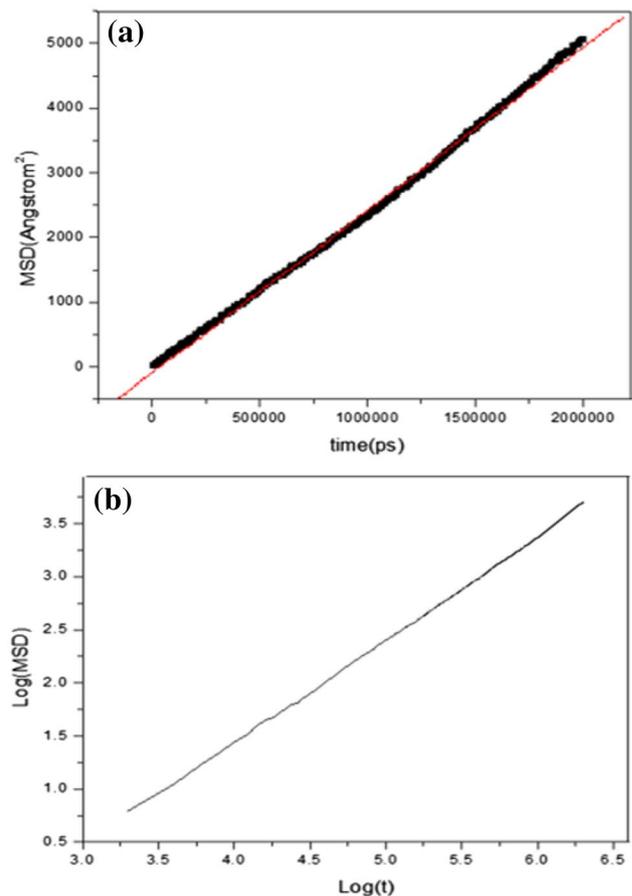


Fig. 4 Mean square displacement of bulk water (a) and β plot (b) $D = 2.5E-9 \frac{m^2}{s}$; $EXP = 2.3E-9 \frac{m^2}{s}$

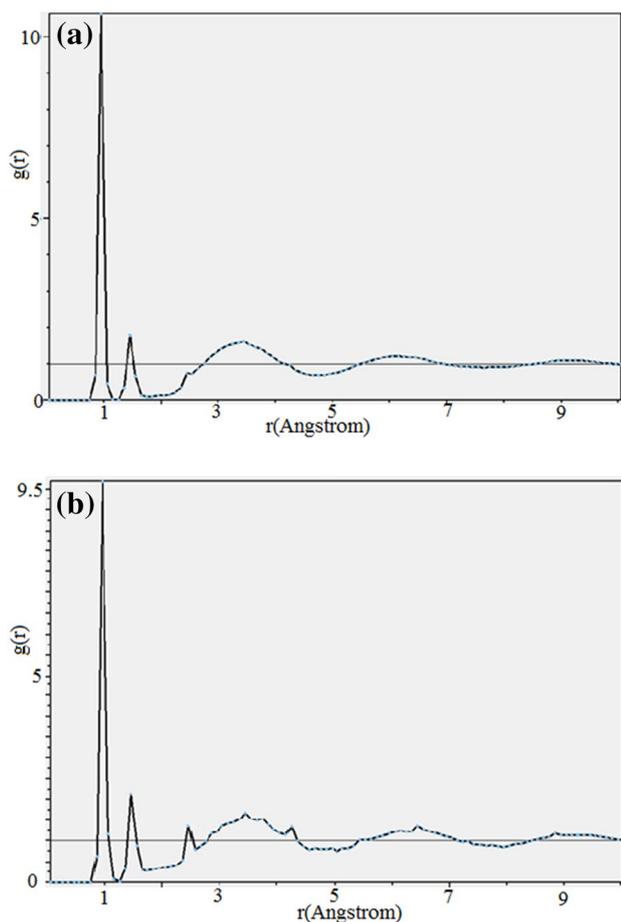


Fig. 5 The RDF of **a** 20×20 graphene sheet and **b** 10×10 graphene sheet

The effect of size is generally rather difficult to measure and the literatures are still relatively small. These calculations give good inside about phenomena’s happen in the atomic level and help to engineer particle size for viscosity control.

3 Conclusion

In this study, the effect of volume concentration on the viscosity of graphene/water nanofluid has been studied. The results showed that,

- TIP3P potential is proper for calculating the thermo-physical properties of water.
- All graphene/water fluids have higher viscosity compared to their base fluid (water) for all systems.
- At constant temperature, the viscosity decreases with the increase of graphene sheet size.
- Distinct layers of water molecules are formed at the vicinity of graphene sheet.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Appendix

```

Input file for viscosity calculation
# LAMMPS input script for viscositya
units                real
variable             T equal 298
variable             V equal vol
variable             dt equal 4.0
variable             p equal 400                # correlation
                                                length
variable             s equal 5                 # sample interval
variable             d equal $p*$s            # dump interval
# convert from LAMMPS real units to SI
variable             kB equal 1.3806504e-23   # [J/K/Boltzmann
variable             atm2 Pa equal 101325.0
variable             A2 m equal 1.0e-10
variable             fs2 s equal 1.0e-15
variable             convert equal ${atm2 Pa
                    }*${atm2 Pa}*${fs2 s}*${
                    A2 m}*${A2 m}*${A2 m}

# setup problem
# equilibration and thermalization
neigh_modify         delay 0 every 1 check yes
fix                  fxnvt all nvt temp 298.0
                    298.0 120 iso 1.0 1.0
                    1000.0 drag 1.0

thermo               100
#thermo_modify flush yes
dump 3                all custom                100 dump.xyz x
                    y z q

run                  1000000
write_data            system_after_nvt.data
unfix fxnvt
undump 3
restart 1000 m mahnaz
reset_timestep 0
variable             pxy equal pxy
variable             pxz equal pxz
variable             pyz equal pyz
fix                  SS all ave/correlate $s   v_pxy v_pxz
                    $p $d &                    v_pyz type auto
                                                file S0St.dat ave
                                                running
    
```

```

variable      scale equal ${convert}/
              (${kB}*T)*V*$s*${dt}
variable      v11 equal trap(f_
              SS[3])*${scale}
variable      v22 equal trap(f_
              SS[4])*${scale}
variable      v33 equal trap(f_
              SS[5])*${scale}
thermo_style custom step temp press v_pxy v_pxz v_pyz v_v11
              v_v22 v_v33
run           100000
variable      v equal (v_v11+v_
              v22+v_v33)/3.0
variable      ndens equal count(all)/
              vol
print         "average viscosity: $v
              [Pa.s/@ $T K, ${ndens}/
              A^3"
Input file of potential:
pair_coeff 1   1 lj/cut/coul/long 0.07
              3.55
pair_coeff 2   2 lj/cut/coul/long 0.03
              2.42
bond_coeff 1   harmonic 469.0 1.4
bond_coeff 2   harmonic 367.0 1.08
angle_coeff 1  harmonic 63.0 120.0
angle_coeff 2  harmonic 35.0 120.0
dihedral_coeff 1  opls 0.0 7.25 0.0 0.0
dihedral_coeff 2  opls 0.0 7.25 0.0 0.0
dihedral_coeff 3  opls 0.0 7.25 0.0 0.0
dihedral_coeff 4  opls 0.0 7.25 0.0 0.0
dihedral_coeff 5  opls 0.0 7.25 0.0 0.0
dihedral_coeff 6  opls 0.0 7.25 0.0 0.0
improper_coeff 1  harmonic 2.5 0

```

^a<https://lammps.sandia.gov/doc/Manual.html>

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