Molecular dynamics simulation study on viscosity of silver nanoparticle printing ink

Sha Li\(^2\)\(^,*\), Lu Gao\(^1\), and Hao Liu\(^1\)

\(^1\)School of Textile Science and Engineering, Tiangong University, Tianjin, China
\(^2\)School of Mechanical Engineering, Tiangong University, Tianjin, China

*Corresponding author: lisha@tiangong.edu.cn

Abstract. Ink-jet printing and ink direct writing technologies show great advantages in printing electronics and structural customization of flexible materials. The viscosity of the ink will affect the flow rate of the working medium, is an important parameter in the process of deposition. In this paper, the research status of metal particle printing ink and its rheological properties were briefly introduced. Then, water-based silver nanoparticle ink was selected as the research object, and the base liquid system was established with the TIP4P/2005 water model. The shear viscosity of the base liquid was calculated, and the accuracy of the water model in predicting the viscosity was verified. Considering the size of the silver nanoparticles, volume fraction and temperature of the three factors on the viscosity, the effects of the equilibrium molecular dynamics based on Green-Kubo formula viscosity calculation method under different conditions was calculated respectively set shear viscosity of the ink, the conclusion is temperature, volume fraction and particle size on the shear viscosity value, viscosity values associated with negative temperature, volume fraction and the viscosity value is a positive correlation, and particle size has less effect on the viscosity, particle decreases, and the viscosity value increased slightly.

Keywords: printing ink, rheological properties, Shear viscosity, Molecular dynamics, nanofluids.

1. Introduction
The additive manufacturing of flexible materials reduces the time needed to prototype and explore new structural characteristics [1-2]. Compared with the traditional manufacturing method, this new manufacturing method also has great advantages in reducing the waste of raw materials, saving economic costs, and improving production efficiency. The emergence of nanoparticle inks has promoted the development of 3D printing electronic products. These inks are colloidal suspensions [3-4] prepared by dispersing different nanoparticles into conventional fluids. Particle types can be metals, metal oxides, functional materials, conductive ceramics, etc.

Silver has the best electrical and thermal conductivity among metals, as well as remarkable antibacterial properties, and has been widely used in many fields such as electricity, optics, and biology [5]. Silver nanoparticle inks can be deposited on the flexible substrate by inkjet printers to produce microelectrodes [6], conductive patterns [7], patch antennas [8], radio frequency identification
tags and other applications. The manufactured products have the advantage of smaller dimensional deformation and are selected as processing materials by various additive manufacturing technologies. In the process of fluid deposition, the viscosity coefficient determines the mechanical parameters in the extrusion process, such as the extrusion force and flow rate. In this regard, researchers have carried out a series of numerical simulation research and experimental exploration. Razmara, N. and H.Namarvari [10] studied the viscosity of single-walled carbon nanotube fluids based on water, and simulated the effects of volume fraction and temperature on the viscosity with the green-Kubo method, and established the correlation model. Izadkhah, M. and S.Z.Heris[11] studied the stability and viscosity of contact between the base fluid of water and ethylene glycol with alumina nanoparticles in different proportions, and the results showed that molecular dynamics correctly predicted the viscosity of nanofluids at different temperatures, concentrations and base fluid types. Khaledialidusti, R. and E. Mahdavi [12] assessed the stability of two-dimensional graphene dispersion in liquid carbon dioxide and concluded that increasing the uniformity of nanosheet dispersion could improve the viscosity.

From the above discussion, it can be seen that the parameters affecting the viscosity of nanofluids mainly include the type of base fluid, temperature, particle concentration, and particle size. However, due to the lack of a variety of influencing factors on the viscosity of water-based silver nanoparticle ink, there is a great shortage in the precision control of fluid, which limits the structure customization with high accuracy requirements in additive manufacturing. In addition, using experimental methods to conduct research at the nanoscale has strict requirements on experimental conditions, the particle size is difficult to control, and it is easy to produce large experimental errors. Molecular dynamics simulation can simulate the microscopic evolution process of the fluid system on the atomic scale and obtain thermodynamic information. It is an effective numerical method for studying thermal physical properties. Therefore, the effects of temperature, particle diameter, and mass fraction on the shear viscosity of water-based silver nano printing ink were investigated by means of equilibrium molecular dynamics method in this paper, so as to provide a reference for the processing of nanofluid.

2. Model construction and calculation method

2.1. Model building

Water is widely used in industrial production and life, in order to make the water in the different system of molecular dynamics simulation to get accurate results, the researchers have developed a variety of water model to calculate the chemical, they are on the bond length, bond Angle, take charge and points some discrepancies [13], this article selects four rigid model TIP4P/2005 [14] to describe the role of the relationship between water molecules. At the same time, the nanofluid physical model was constructed by mixing spherical particles with water molecules. The water molecules are arranged around the particles according to the face-centered cubic. Considering the density of water at 1 standard atmospheric pressure is 1g/cm³, the length of the simulated box constructed by 1000 water molecules and nanoparticles with the particle size of 5Å is 34Å. As shown in Figure 1:

![Figure 1. Ag-H2O nanofluids model.](image_url)
2.2. The simulation method

There are two molecular dynamics methods for calculating shear viscosity: equilibrium method and non-equilibrium method. The equilibrium molecular dynamics method is easy to maintain the stability of the system. Therefore, the equilibrium molecular dynamics method (EMD) is adopted. The principle of viscosity calculation in this method is the Green-Kubo relation based on fluctuation-dissipation theorem [15], which is obtained by integrating the autocorrelation function of off-diagonal elements of the pressure tensor, as shown in Equation (1):

$$
\eta = \frac{V}{k_BT} \int_0^\tau \langle P_{\alpha\beta}(0) P_{\alpha\beta}(0) \rangle dt
$$

where $\eta$ is the shear viscosity, $V$ is the system volume, $k_B$ is Boltzmann's constant, $T$ is the system temperature, angle brackets represent the ensemble average, $\tau$ is the correlation length, $P_{\alpha\beta}$ is the off-diagonal element of the pressure tensor, $m_i$ is the mass of the atom $i$ and $v_j$ is the speed, as shown in Equation (2):

$$
P_{\alpha\beta} = \frac{1}{V} \sum_{i=1}^{N} m_i v_{i\alpha} v_{i\beta} + \frac{1}{V} \sum_{i=1}^{N} \sum_{\gamma=1}^{N} f_{\alpha\gamma} f_{\beta\gamma}
$$

Morse potential [16] is used between silver and silver, expressed as Equation (3), where $D_0 = 7.66 \text{kcal/mol}$, $r_0 = 3.155 \text{ Å}$, $\alpha = 1.369 \text{Å}^{-1}$. The 12-6 Lennard–Jones potential with long-range coulomb interaction term describes the force between water molecules and water molecules and silver atoms, as shown in Equation (4), and the corresponding force field parameters are shown in Table 1.

$$
u_{\text{Morse}} = D_0 \left[ e^{-2\alpha(r-r_0)} - 2e^{-\alpha(r-r_0)} \right]
$$

$$
u_{\text{water}} = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \sum_{i,j=\text{w}} q_i q_j \frac{1}{r_{ij}}
$$

|        | H-Ag | O-Ag | O-O |
|--------|------|------|-----|
| $\epsilon(\text{kcal/mol})$ | 0.542 | 0.542 | 0.1582 |
| $\sigma(\text{Å})$ | 2.5 | 2.68 | 3.1589 |

The Velocity-Verlet algorithm is adopted to solve the motion equation, and Nose-Hoover hot bath and pressure bath are adopted [17]. The integral time step as 1fs. First, 200ps was relaxed under the canonical ensemble to make the system reach the specified temperature, and then 400ps was run under the NPT ensemble to reach the required pressure so that the energy fluctuation of the system could reach stability. Finally, 1ns time was used to collect data. During this period, the SHAKE algorithm [18] was used to control the structure of water molecules, and the PPPM method [19] was used to solve the long-range coulomb force with a solution accuracy of 1/10000. The off-diagonal components of the pressure tensor are output to the file for every 5fs, and the autocorrelation function is calculated to obtain the viscosity coefficient. Periodic boundary conditions are used in all three directions to control the volume fraction by adjusting the size of silver particles and the number of water molecules. LAMMPS simulation program was used for all calculations [20].
3. Results and analysis
Before calculating the viscosity of nanofluids, the viscosity of water-based liquid was calculated and compared with the experimental values, to verify the correctness of the calculation method and the rationality of the confirmation of the model. The simulation was carried out within the temperature range of 283-333K, and the results are shown in Figure 2. As can be seen from the figure, the pressure self-correlation function fluctuates violently in the first few picoseconds and then decreases to 0 at 3ps with the convergence of the integral. The calculated results of viscosity and density are consistent with the reference values, and the maximum relative errors are 13% and 1.1%, respectively. Therefore, the TIP4P/2005 water molecular model can accurately predict the shear viscosity of water.

![Figure 2](image1.png)

**Figure 2.** The change of autocorrelation function and viscosity value of water-based liquid(a) and nanofluids(b) with simulation time at 283K

![Figure 3](image2.png)

**Figure 3.** (a) Comparison of calculated and experimental values of viscosity and density of water-based solution.(b) Comparison of viscosity values between aqueous and nanofluids at different temperatures

Figure 2 shows the change of the pressure autocorrelation function curve and the viscosity coefficient of the nanofluids model with a particle volume fraction of 2.4% at 283K. Similar to the water-based liquid, the pressure autocorrelation function decuples to around 0 aftershocks, indicating that the correlation time of the system is 3.5ps and the viscosity is stable at 1.3mpa·s. The viscosity of nanofluids at different temperatures is similar to that of water and decreases with increasing temperature. This is because atoms move faster at higher temperatures, reducing the resistance to
movement between them. The lower temperature has a great influence on the rate of viscosity decline. The viscosity decreases by 35% within the temperature range of 283K-303K, while it decreases by 16.4% within the temperature range of 313K-303K. Relative viscosity is defined as the ratio of the nanofluids viscosity and fluid viscosity, the research on the viscosity of nanofluids, this definition is often used to eliminate the base effect, its value changes instability, under the different temperature range, relative to the base fluid, add significantly increase the viscosity of the fluid particles, and stable growth has nothing to do with the temperature increase of viscosity.

Figure 4. (a) Relative viscosity. (b) Viscosity comparison of nanofluids with different particle sizes. (c) Viscosity contrast at different volume fractions

Temperature and particle size have a great influence on shear viscosity value, and different application scenarios have different requirements on fluid-particle concentration. Therefore, it is necessary to explore the influence of volume fraction on viscosity value. The nanofluids system was constructed with a particle size of 5A, and the viscosity was calculated at different volume fractions of 1.4%, 2.4%, 3.4%, and 4.4%, respectively, at 313K. As can be seen from fig.8, the shear viscosity value increases with the increase of volume fraction, grows slowly at low concentration, but increases greatly at high concentration. When the volume fraction is 3.4%, it increases greatly compared with 2.4%.
4. Conclusions
The shear viscosity value of water-based silver nanoparticle ink was calculated by using the equilibrium molecular dynamics method based on the Green-Kubo formula, and the factors affecting the viscosity value of nanoparticles were revealed, which is of great significance for the study of nanofluids. This facilitates the application and preparation of nanofluids in the engineering field. The results show that TIP4P/2005 is an effective model for predicting viscosity. The particles significantly increase the viscosity of the fluid. At the same particle size and concentration, the viscosity has a strong correlation with temperature, and the viscosity decreases with the increase of temperature. At the same temperature and particle concentration, the viscosity decreases with the increase of particle size. At the same temperature and particle size, the viscosity of nanofluids increased with the increase of particle concentration, and at high particle concentration, the increase of viscosity was more significant, which proved that the increase of viscosity had a great correlation with the contact area between particles and water.

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