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Dependence of the viscosity of nanofluids on nanoparticle size and material

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ABSTRACT

The viscosity of nanofluids as a function of nanoparticle size and material is modeled and analyzed. Dependences of the viscosity of nanofluids based on liquid argon with aluminum and lithium nanoparticles are obtained. The nanoparticle size ranges from 1 to 4 nm. The volume concentration of nanoparticles is varied from 1% to 12%. It is shown that the viscosity of the nanofluid increases with decreasing nanoparticle size and, in addition, depends on the nanoparticle material.

1. Introduction

A nanofluid is a two-phase system consisting of a carrier fluid and nanoparticles. Even today it can be argued that nanofluids are a very promising material. They have been used or are planned to be used in a variety of chemical reactors and plants, including catalytic ones, for cooling various devices, in the development of new systems of heat production and transportation, in biotechnology, nanotechnology, and microelectromechanical systems (MEMS) for various purposes, in the design of new drugs and cosmetic products, for the delivery of drugs, in the development of systems for detecting various contaminants and cleaning air and water, in the development of new lubricants, paints, varnishes, construction materials, etc.

The specific small sizes of nanoparticles are responsible for their very special properties. Due to this, nanofluids also have special properties which cannot be described by classical theories. Since nearly all applications of nanofluids are related to channel flows, viscosity is a determining factor in their use. The considerable practical importance of this problem has led several dozen research groups in different countries to undertake experimental studies of the viscosity of nanofluids over the last ten to fifteen years (see reviews [1–3]). It has been well established that the viscosity of nanofluids is much higher than the viscosity of conventional dispersions at equal volume concentrations of dispersed particles and is not described by any classical theory of the viscosity of these fluids (Einstein, Batchelor, Mooney Akrivos and Chang, Krieger, etc.). It has further been found that the effective viscosity of nanofluids depends not only on the concentration of nanoparticles, but also on their size. Evidence for this has been provided by molecular dynamics simulations for the hard-sphere potential [4,5] as well as by experiments [3,6–8]. Recent studies have shown that at a given nanoparticle concentration, the viscosity of nanofluids increases with decreasing nanoparticle size. However, opposite data have also been reported [9,10]. Thus, the question of how the viscosity of nanofluids depends on the nanoparticle size is still relevant. Answering this question is the first objective of this work.

Obtaining experimental data on the viscosity of nanofluids is complicated by several factors: difficulties in producing monodisperse suspensions, various methodical problems of accurate measurement of particle size, concentration, uniformity of size distribution, the formation of agglomerated particles, etc. An ideal experiment with a monodisperse nanofluid can be performed using molecular dynamics (MD) simulation of its viscosity. It is this method which is used in the present work to simulate the shear viscosity of nanofluids. However, unlike in [4,5], here we use real interaction potentials, and not the hard-sphere potential.

In [3], it is noted that the viscosity of nanofluids may also depend on the nanoparticle material. This correlates with the data of the kinetic theory of gas nanosuspensions where this dependence has been well established [11,12]. The first MD calculations have confirmed the existence of this dependence [13]. Obtaining systematic data that would give an unambiguous answer to the question of the dependence of the viscosity of nanofluids on the nanoparticle material is the second objective of this paper. We

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studied the viscosity of model nanofluids in which the carrier fluid was argon of density $\rho = 0.707$ and temperature $T = 300$ K. The dispersed component was lithium and aluminum nanoparticles with a diameter from one to four nanometers. The number of argon molecules in the simulation cell was varied from 7000 to 14,800, and the number of nanoparticles from 1 to 64. The volume concentration of nanoparticles was varied from 1% to 12%. The obtained data were averaged over 2000 independent phase trajectories. The typical computation time for a single point on a personal computer (single-core Intel Core 2) was about 500 h. The computational complexity and time naturally increases with increasing number of molecules and nanoparticles in the simulation cell and with increasing size and mass of nanoparticles.

2. Simulation technique

In the simulation, we employed a standard molecular dynamics method (see, e.g., [14,15]). A cubic cell and periodic boundary conditions were used. Interaction between the molecules of the carrier fluid was described by the Lennard–Jones potential

$$\Phi_{LJ}(r) = 4\varepsilon\left[(\sigma/r)^{12} - (\sigma/r)^{6}\right], \tag{1}$$

where σ is the effective diameter of the fluid molecules, ε is the depth of the potential well, and $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between molecules i and j.

Interaction between carrier–fluid molecules and a nanoparticle was described by the Rudyak–Krasnolutskii (RK) potential [16,17].

$$\begin{aligned}
&\Psi(r) = \Psi_9(r) - \Psi_3(r),\\
&\Psi_i = C_i\left\{\left[\frac{1}{(r-R)^i} - \frac{1}{(r+R)^i}\right]\right.\\
&\qquad \left. - \frac{a_i}{r}\left[\frac{1}{(r-R)^{i-1}} - \frac{1}{(r+R)^{i-1}}\right]\right\},
\end{aligned} \tag{2}$$

where $i = 9, 3$, $a_9 = 9/8$, $a_3 = 3/2$, $C_9 = (4\pi\varepsilon_{12}\sigma_{12}^{12})/45V_p$, $C_3 = (2\pi\varepsilon_{12}\sigma_{12}^{6})/3V_p$, $V_p^{-1} = \rho_p/m_p$. Here ρ_p is the density of the nanoparticle material, m_p is the mass of the molecule (atom) of the nanoparticle, R is the radius of the nanoparticle, $\sigma_{ij}, \varepsilon_{ij}$ are the parameters of the interaction potential (1) between a carrier–fluid molecule and a molecule of the nanoparticle.

As the nanoparticle interaction potential we use a specially constructed potential [18], which for monodisperse nanoparticles has the form

$$U(r,R) = U_7(r,R) - U_1(r,R), \tag{3}$$

where

$$\begin{aligned}
U_7(r,R) = {}& \frac{\pi^2}{315}\frac{\tilde{\varepsilon}\tilde{\sigma}^{12}}{V_p^2}\left\{\frac{R^2}{r}\left[\frac{1}{(r-2R)^7} + \frac{2}{r^7} + \frac{1}{(r+2R)^7}\right]\right.\\
& - \frac{R}{3r}\left[\frac{1}{(r-2R)^6} - \frac{1}{(r+2R)^6}\right]\\
& \left. - \frac{1}{30r}\left[\frac{1}{(r-2R)^5} - \frac{2}{r^5} + \frac{1}{(r+2R)^5}\right]\right\},\\
U_1(r,R) = {}& \frac{2\pi^2}{3}\frac{\tilde{\varepsilon}\tilde{\sigma}^{6}}{V_p^2}\left[\ln\left(\frac{r^2-4R^2}{r^2}\right) + 2R^2\left(\frac{1}{r^2-4R^2} + \frac{1}{r^2}\right)\right].
\end{aligned}$$

Here R is the radius of the nanoparticles, $\tilde{\varepsilon}$ and $\tilde{\sigma}$ are the parameters of the Lennard–Jones (1) interaction potential of the nanoparticle molecules.

Potentials (2) and (3) were constructed under the assumption that the interaction between the carrier–fluid molecules and nanoparticle molecules and the interaction of the nanoparticle molecules form are described by potential (1), respectively, with the parameters σ_{12}, ε_{12} and $\tilde{\sigma}$, $\tilde{\varepsilon}$. The simulation was performed as follows. Carrier–fluid molecules and nanoparticles were uniformly placed in the simulation cell according to the specified values of the density of the carrier–fluid and the volume concentration of nanoparticles. The density of the pure fluid was determined by the parameters: $\rho = N\sigma^3/V$ and $\alpha = V/V_0$, where V is the volume of the system (cell), $V_0 = N\sigma^3/\sqrt{2}$ is the volume of close packing of N molecules. The volume of the simulation cell for the nanofluid was given by the relation $V = \alpha N_1\sigma^3/\sqrt{2} + 4\pi k_V N_2 R^3/3$, where N_1 and N_2 are the number of molecules and nanoparticles, respectively. With the addition of nanoparticles, the coefficient k_V was chosen so that the nanofluid pressure was equal to the pressure of pure argon of the given density.

The initial velocities of molecules were specified according to the Maxwell distribution at the given temperature, and those of nanoparticles were set equal to zero. The calculation was started after an initial relaxation period, during which the whole system had come to equilibrium. The Newton equations were integrated using Schofield's scheme [19].

Since the potentials used here have an infinite range, they should be truncated during the simulation. For potential (1), the truncation radius was 2.5σ, and for potential (2), it was $(R + b\sigma_{12})$. The value of b was chosen so that at the truncation radius for potential (2), the force exerted on a molecule by a nanoparticle was equal to the force of interaction between two molecules at the truncation radius for potential (1). The quantity b depends on the nanoparticle radius, material and the properties of the carrier–fluid molecules. In particular, for Li nanoparticles (for the diameter of the nanoparticles was 2 nm) in Ar, b was equal to 3.78, and for Al nanoparticles, it was 4.02. The nanoparticle interaction potential was truncated at a distance at which the interaction force between nanoparticles was zero, i.e., the so-called soft-sphere potential was used.

It should be noted that the simulation of the evolution of nanofluids imposes more severe restrictions on the size of the simulation cell as compared with homogeneous fluids. Since a nanoparticle should not interact with itself, the side length of the cubic cell L should be much greater than the range of the potential $L \gg \tilde{R}$. In practice, the distance should be, at least, several times greater to avoid the corresponding correlations.

The parameters of the interaction potential of argon molecules were as follows: $\sigma = 3.405$ Å and $\varepsilon/k_B = 119.8$ K [20]. The parameters of potentials (2) and (3) were calculated using the following parameters of potential (1): for lithium, $\sigma = 3.95$ Å and $\varepsilon/k_B = 500$ K [21], and for aluminum, $\sigma = 2.551$ Å and $\varepsilon/k_B = 857.6$ K. The latter parameters were obtained from data on Young's modulus and the structure of the crystal lattice (face-centered cubic) using a method similar to that described in [22]. The parameters σ_{12} and ε_{12} were determined using the simple combinational relations: $\sigma_{12} = \sqrt{\sigma\tilde{\sigma}}$ and $\varepsilon_{12} = \sqrt{\varepsilon\tilde{\varepsilon}}$.

Shear viscosity was calculated from the Green–Kubo formula [23]

$$\begin{aligned}
\eta = {}& \frac{V}{3k_BT}\int_0^{\tau}\big\langle J_{xy}(t)J_{xy}(t+t_1) + J_{yz}(t)J_{yz}(t+t_1)\\
& + J_{zx}(t)J_{zx}(t+t_1)\big\rangle dt_1,
\end{aligned} \tag{4}$$

where the xy component of the stress tensor for a binary mixture has the form

$$\begin{aligned}
J_{xy} = {}& \frac{1}{V}\left[\sum_{\alpha=1}^{2}\sum_{i=1}^{N_\alpha} m_\alpha \dot{x}_i\dot{y}_i + \frac{1}{2}\sum_{\alpha=1,i\neq j}^{N_1} F_{x,ij}y_{ij}\right.\\
& \left. + \frac{1}{2}\sum_{\alpha=2,i\neq j}^{N_2} F_{x,ij}y_{ij} + \sum_{i=1}^{N_1}\sum_{j=1}^{N_2} F_{x,ij}y_{ij}\right].
\end{aligned} \tag{5}$$