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Effect of temperature and diameter of narrow single-walled carbon nanotubes on the viscosity of nanofluid: A molecular dynamics study

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ABSTRACT

Equilibrium molecular dynamics simulations by all-atom model have been employed to investigate the adsorption properties and temperature dependence of the shear viscosity of ethanol molecules confined in narrow single-walled carbon nanotubes (SWCNTs). Since the properties of the narrow tubes (diameters < 7 Å) are strongly influenced by their curvature, the narrow SWCNTs with diameters ranging from 0.54 to 1.08 nm and the length of 2.5 nm in ethanol reservoir at 273.0, 298.0 and 323K and 1 bar have been studied. The results indicate that endo-adsorption occurs in nanotubes with the diameter larger than 0.81 nm and as a result ethanol nano-wires can be formed inside nanotubes.

Calculations of shear viscosity of the nanofluid using Green–Kubo method reveal that the relative viscosity of the confined ethanol decreases with increasing temperature.

All the CNT@ethanol fluids have lower viscosity than the base liquid ethanol at all temperatures and the viscosity increases with the increase of CNT radius and endo-adsorption.

Chirality of the CNTs has minor effects on shear viscosity and endo-adsorption and the main factor is CNTs diameter.

The results of the present work provide deep understanding of the viscosity changes with temperature at the nanofluids and can describe the mechanisms for base fluid property modifications caused by adding nanoparticles. These results are applicable in design and preparation of diesohols and fuel-grade ethanol.

1. Introduction

Nanofluids are suspensions of solid nanometer-sized particles, with average sizes on the order of 1–100 nm dispersed in various conventional base liquids [1]. The nanoparticles are usually carbides, metals, oxides, or carbon nanotubes while the base liquids can be made of water, acetone, ethanol, toluene or glycol. Suspended nanoparticles often modify the thermophysical properties of the base liquid dramatically, although they are in the trivial amount in the fluid. In recent years, nanofluids have attracted much attention because of their promising properties such as anomalously large thermal properties, improved viscosity, tunable surface tension, and rheology behavior [2–4]. These properties strongly affect the application of nanofluids such as lubrication, electronic-cooling and biomedical systems [5,6].

Molecules confined in the nanopore are now of exceptional interest duo to their unusual properties [7] and high importance for industrial applications [8] such as molecular detection, gas storage [9] and membrane separation [10].

There are experimental and theoretical studies of fluids confined in nanotubes. To our knowledge, Gordillo and Marti [11] presented the first MD report of water in CNTs and followed by many others [12].

Most reports focused on the behavior of a pure and simple fluids like hydrogen [13], argon [14], helium [14], neon [15], methane [16], ethane [16], ethylene [16] or water confined in simpler nanopores [17].

Water confined in single-walled carbon nanotubes (SWCNTs) has been paid much attention in recent years [18,19]. Many researchers investigated the structure and flow behavior of water molecules confined in CNTs with experimental and MD simulations

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methods.

Ethanol is an important fluid in chemical and biological processes. The behavior of alcohol in nanopores and other ion-channels is related to the behavior of ethanol molecules inside the channel pore and causes many influences in humans. On the other hand, ethanol behavior within the nanopore is important for the production of fuel-grade ethanol and application of ethanol in diesohols (diesel–ethanol blends) that now has become a popular fuel [20,21].

Thermo physical properties of complex liquids played an important role in both system design and optimization [22]. Many researchers have studied the viscosity temperature dependence of hydrocarbon compounds and fluids. Mondello and Grest [23] used equilibrium molecular dynamics to calculate viscosity and dynamics of *n*-alkanes [24].

So far, the viscosity of confined liquids in nano confinement has been explored seldom due to their small scales (comparable to the molecular diameter). In this situation, the transport properties are extremely difficult to be investigated by experiments. There are a large number of published articles on thermal conductivity [25,26] however only a little report on deriving the nanofluid viscosity and rheology from experimental and theoretical point of views, which limits the application and development of nanofluids.

Molecular dynamics simulation is the most effective way to describe, understand and predict the details of a structure, thermodynamic properties and many fundamental relatively complex nanofluid problems. Molecular dynamics is based on analysis of interactions (using various pair atomic force fields) and atom dynamics.

In this work, equilibrium molecular dynamics simulations have been performed in order to investigate the effect of CNT diameter and chirality on the adsorption properties of confined ethanol molecules. We also investigate how nanoparticles alter the viscosity of nanofluids from microscopic viewpoint. Narrow SWCNTs have been used as a model because in narrow CNTs the curvature effects are important and they are as small as ion-channels and can be studied as a prototype for the complicated 1-dimensional (1D) nanopores. In addition, the effect of temperature on the viscosity has been investigated which can be helpful in designing and preparation of “smart materials”.

2. Computational method

Many researchers have used molecular dynamics (MD) simulation to study the viscosity temperature dependence of hydrocarbon compounds and fluids. There are two widely used molecular dynamics methods for determining thermodynamic properties of fluids: equilibrium molecular dynamics (EMD) simulation i.e., the Green–Kubo (GK) method and nonequilibrium molecular dynamics simulation (NEMD) [27–29]. The GK method is a well-established technique in the physics [30] chemistry [31] and mathematics communities [32] and is widely used for determining viscosity in nanofluids.

In GK 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 [33]. GK method suffers from the poor convergence of the correlation function that results in inaccurate estimates. However, by using sufficient statistics with a careful choice of integration time, this drawback of EMD is overcome [34,35]. EMD is a multi-property method that all thermodynamic properties can be calculated at the same state point from a single simulation run and does not suffer from additional adjustments that the nonequilibrium method usually needs.

On the other hand, in the GK method no driving force is imposed on the simulation system and as a result, it will always be in the linear response regime and it is one of the most important advantages in using GK approach compared with the NEMD method. These advantages of EMD method have then drawn our attention and the shear viscosity using GK method is computed according to

$$\eta = \frac{V}{3k_BT}\int_0^\infty < \sum_{x<y} P_{xy}(t)P_{xy}(0) > \mathrm{d}t \qquad (1)$$

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} refers to an independent component of the pressure (stress) in the xy direction [36]. The integrand is the autocorrelation function of the pressure tensor P. The GK formulation utilizes a single summation that consolidates the contributions of all the atoms into a single autocorrelation function($C_{xy}(t)$).

2.1. Ethanol molecule

Monte Carlo simulations [37] indicate that the OPLS (optimized potentials for liquid simulations) potentials predict equilibrium and thermodynamic properties of several liquid alcohols are in good agreement with experiments. Polarizable potentials for liquid alcohols also have been recently [38] used for the simulation of the equilibrium and thermodynamic properties of liquid ethanol [38]. The predictions do not show significant differences with OPLS results.

The OPLS potential functions used three kinds of models, all-atom (AA), partially united atom (UA) and anisotropic united atom (AUA) models. In united-atom (UA) model; sites for nonbonded interactions are placed on all non-hydrogen atoms and on hydrogen's attached to heteroatoms or carbons in aromatic rings [39]. Thus, the only hydrogen's that are implicit are attached to aliphatic carbons. In the OPLS all-atom model, every atom of molecule is taken as an individual interaction site. The calculation time in simulations is proportional to the total number of interaction sites; therefore, the AA models are expensive for large systems or molecules [40]. Nevertheless, the added sites in AA models allow more flexibility for torsional energetics and charge distributions. The reported results indicate that AA models for hydrocarbons represent experimental data better than the UA model in several areas. Hence, in the present work we have adopted the AA–OPLS potential for ethanol molecules developed by the Jorgensen group [39].

2.2. Carbon nanotube

Carbon atom in the SWCNT nanotube is treated as a neutral Lennard-Jones (L-J) interaction site [41]. The potential energy of intermolecular interactions is defined as a combination of a L-J12-6 potential and a Coulomb potential

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_iq_j}{r_{ij}} \qquad (2)$$

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 obtained by Lorentz-Berthelot combining rules,

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2, \varepsilon_{ij} = \sqrt{\varepsilon_i\varepsilon_j}$$