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Structural and transport properties and solubility parameter of graphene/glycerol nanofluids: A molecular dynamics simulation study

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ABSTRACT

We performed molecular dynamics simulations to calculate the viscosity of graphene/glycerol nanofluids. For this purpose, at first we checked the stability of dispersions of pure graphene nanosheets in glycerol by calculating the solubility parameter of pure graphene and pure glycerol. The results showed the solubility parameter of pure graphene with five layers is 37.37 $MPa^{1/2}$ which is close to that of pure glycerol (38.62 $MPa^{1/2}$). Hence, graphene can form a stable dispersion in glycerol. The influence of number of layers of pure graphene on its structural properties was also investigated. The transport properties of graphene/glycerol nanofluids including diffusion coefficient and viscosity were calculated. The diffusion coefficient of graphene/glycerol nanofluids decreases with increasing number of layers of graphene. The calculated viscosity at 293.15 K is close to our experimental value. To the best of our knowledge, this work reports for the first time the solubility parameter of pure graphene and viscosity of graphene/glycerol nanofluids by MD simulation.

1. Introduction

Quantitative predictions of diffusivity and viscosity are of great importance in guiding experiments and improving engineering designs such as molecular sieve operations, catalytic processing of heavy liquid petroleum fractions, gel permeation chromatography, and membrane separation technologies [1]. However, it is quite difficult to obtain the experimental data under extreme conditions because of the complexity of the systems [2].

Nanofluids belong to a new class of fluids with supposedly enhanced thermophysical properties. Nanofluid is a two-phase system consisting of a carrier medium (liquid or gas) and nanoparticles [3]. The number of publications regarding transport properties like viscosity for technically relevant nanofluids that achieve quantitatively accurate results is low [4,5]. To measure the transport properties of a nanofluid, preparation of a stable dispersion is need. The stability of a nanofluid depends on several factors affect the stability of nanofluid, parameters such as size, shape, kind, and concentration of nanoparticles as well as the kind of fluid, temperature, etc. In general, when there is a repulsive electrostatic or steric forces between particles they tend not to settle rapidly [1].

Graphene is a one-atom-thick sheet of sp^2-bonded carbon atoms in a honeycomb crystal lattice [6] with plenty of unique properties such as high values of charge carrier mobility (15,000 $cm^2\ V^{-1}\ s^{-1}$) [7], unique transport performance [8], theoretical specific surface area (2630 $m^2\ g^{-1}$) [9], thermal conductivity (3000–5000 $W\ m^{-1}\ K^{-1}$) [7], and Young's modulus (1 TPa) [10]. Finding a suitable solvent for dispersing graphene is much important. Solvents such as *N*-methylpyrrolidone (NMP) and *N*,*N*′-dimethylformamide (DMF) were experimentally proven to be efficient in dispersing graphene sheets [11–13]. Yang and Wu [14], using MD simulation, explored the interaction between graphene and supercritical CO_2 ($scCO_2$) fluid. They found $scCO_2$ prohibits the graphene aggregation because the confined CO_2 molecules between graphene sheets may induce a dominating repulsion interaction between graphene sheets. Shih et al. [13] investigated dispersion stability of liquid-phase-exfoliated graphene in polar solvents including water, NMP, DMF, dimethyl sulfoxide (DMSO), and γ-butyrolactone (GBL) by molecular dynamics (MD) simulation and kinetic theory of colloid aggregation. They ranked potential solvents according to their ability in dispersing non-functionalized graphene as: NMP ≈ DMSO > DMF > GBL > H_2O.

An understanding of cohesive energy density is very important for predicting the stability of a nanofluid. The cohesive energy density of a material can be quantified in terms of solubility parameter, δ [15]. Solubility parameter is a numerical value indicating relative solvency behavior of a specific solvent [16]. In 1936, Hildebrand [17] proposed square root of cohesive energy density as a numerical value for the solubility parameter of a specific solvent:

$$\delta = \left(\frac{\Delta_{vap}E}{V}\right)^{\frac{1}{2}} \quad (1)$$

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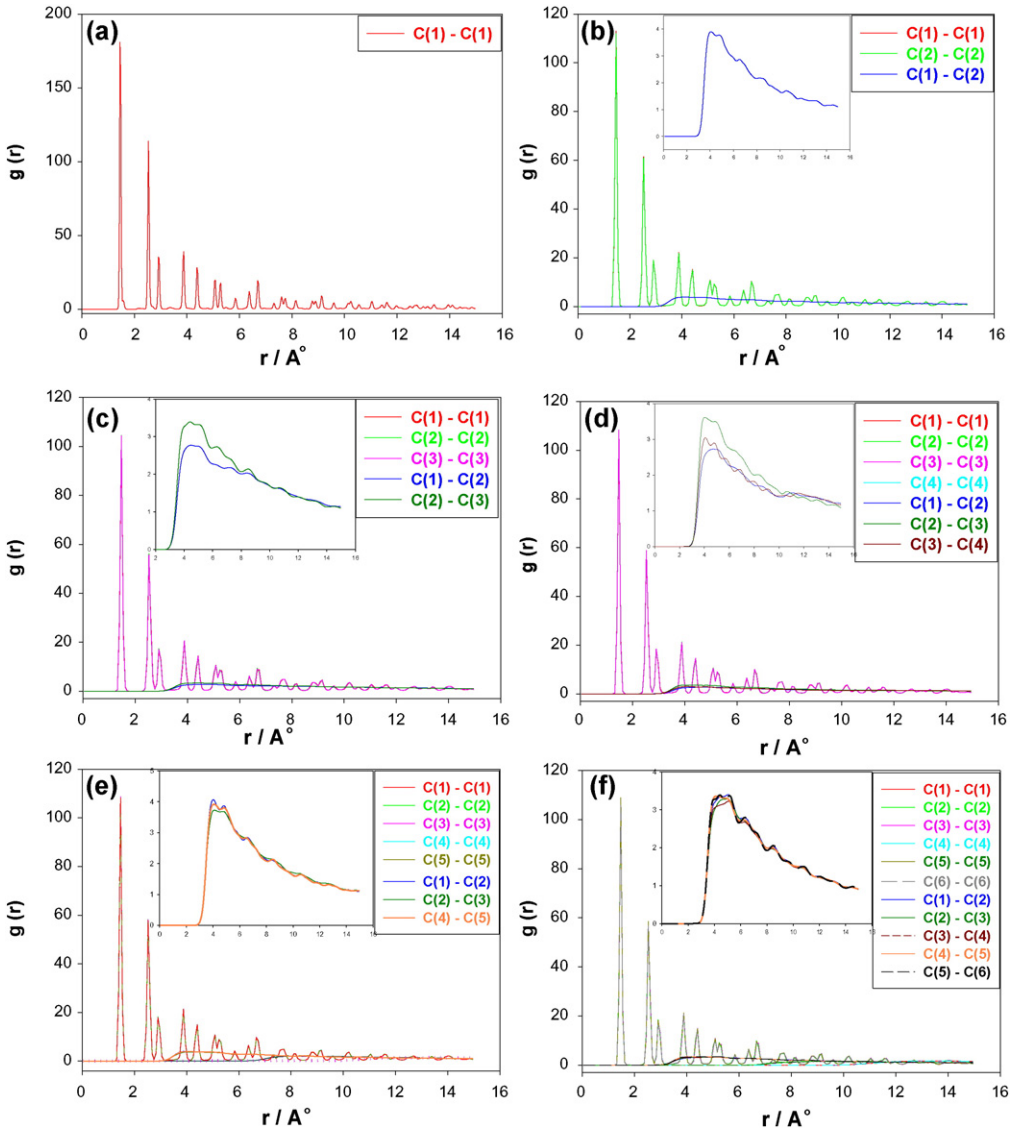

Fig. 1. RDFs of carbon atoms of pure graphene for (a) $N = 1$, (b) $N = 2$, (c) $N = 3$, (d) $N = 4$, (e) $N = 5$, and (f) $N = 6$ at 293.15 K. The insets show the RDFs of carbon atoms placed in the adjacent layers.

where V is bulk volume and $\Delta_{vap}E$ the energy of vaporization. For graphene is defined as [15]:

$$\Delta_{vap}E = E_{bulk} - NE_{molecule} \tag{2}$$

where E_{bulk} and $E_{molecule}$ are the energy of bulk (multilayer) and monolayer graphene, respectively. N stands for number of graphene layers. Hernandez and co-workers [18] showed the solubility parameter and surface tension are most important properties to find efficient solvents for dispersing graphene sheets. Good solvents are those having surface energy or solubility parameter similar to that of graphene. The graphene dispersibility is also maximized in solvents with surface tension close to 40 mJ m^{-2} [11]. Hernandez et al. [18] stated best solvents for graphene should possess $\delta \sim 23$ $MPa^{1/2}$.

The aim of the present paper is to calculate the viscosity of graphene/glycerol nanofluids using MD simulation. For this purpose, at first we need to check the stability the dispersion of pure graphene nanosheets in glycerol as a base fluid. In our previous work, we found that the nanofluid of graphene in glycerol is very stable [19]. In this work, the solubility parameters of pure graphene and pure glycerol are calculated to investigate the stability of graphene/glycerol nanofluids. The influence of number of layers of pure graphene on structural properties and solubility parameter of pure graphene are investigated. Thereafter, the work computes the diffusion coefficient of graphene/glycerol nanofluids in order to calculate the viscosity. The influence of number of layers of graphene on viscosity is investigated. We believe that this study can provide a comprehensive current state-of-the-art in the solubility parameter of pure graphene and viscosity of graphene/glycerol nanofluids. To the best of our knowledge, this work reports the solubility parameter of pure graphene and viscosity of graphene/glycerol nanofluids by MD simulation for the first time.

2. Simulation details

MD simulations were carried out using DL_POLY 2.17 package [20]. The density functional theory performed using GAUSSIAN03 [21] at B3LYP/6-31 g(d) level of theory on glycerol molecule made it possible to access the most stable structure and configuration. In order to be sure that the structure is at local minimum and in its stable form, the vibrational analysis was as well conducted. In addition, atomic charges were derived from natural bond orbital analysis at the same level of theory. The equilibrium parameters containing equilibrium bond lengths, angles, and dihedral angles as well as atomic charges computed were applied for molecular dynamics simulation. The initial structure of