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Molecular dynamics simulation of the effects of affinity of functional groups and particle-size on the behavior of a graphene sheet in nanofluid

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ABSTRACT

The practical application of thermally enhanced nanofluids in automotive industries for higher energy efficiency requires that nanoparticles be buoyant, leading to Brownian motion in the base fluid without aggregation. Numerous studies have reported the long-term stability of dispersions resulting from steric hindrance and an affinity for the surrounding base fluid via modification of nanoparticles with functional groups. In this study, we performed molecular dynamics simulations of nanofluids containing a single graphene sheet with various functional groups to investigate the influence of affinity, as well as particle-size, on the behavior of the graphene sheet. Using the concept of the speed of nanoparticle, we quantitatively evaluated the dependence of behavior on affinity to investigate whether having more functional groups with more attractive interactions has an impact on the stable dispersion in nanofluid. In addition, the simulation results for the particle-size effect revealed that the larger nanoparticles produced more stable dispersion in nanofluid. We concluded that the behavior of the graphene sheet depends on a combination of two factors: different charge assigned to atoms due to a nitrogen atom, and the difference in mass, which influences the speed of the nanoparticles.

1. Introduction

Thermal management is the most critical factor in heat transfer equipment, which can improve the energy efficiency for an economic gain when using fluid. Typically, automotive systems use several working fluids for thermal management such as water, ethylene glycol (EG), propylene glycol, engine oil, mineral oil, kerosene oil, and silicone oil [1]. The coolant, which cools the engine by flowing through the channel, is the most sensitive component with regard to heat transfer efficiency. In an automotive system, hot coolant for heat transfer throughout the engine is cooled when it passes through a radiator [2,3]. Improved cooling at the radiator interface is limited due to its dependence on external air flow. Thus, it is more effective to enhance heat transfer by improving the thermal conductivity of the fluid, which offers the possibility to reduce the size of the radiator, and eventually improve fuel efficiency by reducing the weight of the automobile [2–4]. Generally, this fluid consists of water and EG with a mixing ratio of 1:1 due to the high thermal conductivity of water (0.6 W/m K); EG is used as antifreeze in working environments below 0 °C with its affinity for water [2], although the composition varies with the environment.

A thermal conductivity of coolant of about 0.4 W/m K [5] is a limitation to achieving a higher performance automotive engine [4,6]. Over the past two decades, since the concept of a "nanofluid" was introduced by Choi et al.[7], nanofluids have attracted considerable interest due to their significant enhancements in heat [8] and mass [9] transfer coefficients, as well as improved wetting and spreading [10]. Eastman et al. [11] reported a 40% enhancement in the thermal conductivity of EG by the addition of 0.3 vol % Cu particles, as well as 150% enhancement in the thermal conductivity of synthetic oil using a 1 vol% dispersion of carbon nanotubes.

Nanofluids contain various nano-scale additives, such as metallic nanoparticles [11–13], metallic oxide particles [14,15] and nanotubes [16,17]. Carbon allotropes such as fullerenes, graphene, graphite [18] and carbon nanotubes [19], as well as exfoliated graphite [20] and carbon nanofibers [14,18], are among the most promising candidate materials for additives in nanofluids due to their excellent physical properties. Of these materials, graphene has attracted much interest due to it exceptional physical and chemical properties [20]. Baladin et al. [21] reported that it has outstanding thermal conductivity with long-range ballistic transport at room temperature, and significantly higher thermal conductivity than carbon nanotubes. The phonon thermal

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conductivity of single-layer graphene is in the range of 2000–5000 W/m K, with 775 nm of phonon mean free path [22–24].

Carbon materials including graphene naturally tend to aggregate due to their strong van der Waals interaction [25]. To enhance thermal properties, the dispersion of additives is one of the most critical factors. In particular, the long-term stability of dispersion in nanofluid determines the desired thermal property, such as the degree of enhancement, and even the performance of the system. Several methods [26,27] have been proposed and used, such as surfactant wrapping on the graphene surface, or surface modification by functional groups. Whereas wrapped surfactant needs to be removed after graphene clustering to realize its full thermal properties, surface modification by functional groups requires no post-treatment. Nonetheless, effective dispersion with long-term stability in nanofluid remains a challenge.

To quantitatively define and compare dispersion in nanofluid, Cha et al. [28] suggested the evaluation of dispersion using molecular dynamics simulation by the ratio between the number of single and clustered graphene sheets over time. However, it is possible to maintain dispersion in nanofluid by using functional groups that bond to the surface of the graphene sheet, resulting in steric hindrance and affinity. Simply, it is matter of the interaction between graphene and graphene, or graphene and base fluid. In terms of steric hindrance, the structural behavior of functional groups can help to prevent aggregation [29]. On the other hand, the affinity between nanoparticles and base fluid can affect aggregation or dispersion depending on the type and mass of the functional groups; however, the effects of the type and mass fraction of functional groups has not been quantitated.

Good dispersion of nanoparticles facilitates large enhancements in thermal conductivity compared to using the base fluid alone [30]. Whereas micro-size particles can be affected by gravity, such that they eventually sink into the channels of a system, nano-size particles in the range of 20–50 nm are largely free from the effects of gravity. However, once nanoparticles aggregate, the nanoparticle cluster behaves as a micro-sized particle, which may lead to system malfunction. In addition, the migration phenomenon on the thermal boundary layer in flowing fluid also affects the effectiveness of heat transfer [31].

In this study, we conducted molecular dynamics simulations to investigate the influence of the type and mass fraction of functional groups on the behavior of a graphene sheet in nanofluid, which is one of the most important factors for dispersion. We also investigated the dependence of the behavior on the size of nanoparticles. Base fluids consisting of water and EG (i.e., almost the same configuration as a typical automotive coolant) contain a single graphene with various numbers of functional groups. Two types of functional group were used in this simulation (alkanol and alkanol amine). Further, we employed three patterns of functional group bonding to various-sized graphene sheets to examine the effect of size on the behavior.

2. Simulation method

A mixture of EG and water, with a mass ratio of 1:1, was used as the base fluid for all simulations in this study. We constructed the simulation model with three dimensional periodic structures of water, EG, and graphene sheets with or without functional groups using the software package Materials Studio 2016 (BIOVIA Software Inc., San Diego, CA, USA) [32,33] and carried out the simulations using COMPASS (*Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies*), the force field contained in the package. The density of all the cases in this study is constant at 1.00 g/cm^3 reflected that of a real coolant in the range 1.0–1.1 g/cm^3 due to the mixing ratio by environment. The simulations were performed in two ways for evaluating the effect of parameters of functional group and graphene sheet as follows.

First, we evaluated the effect of the number and type of functional groups bonded to a graphene sheet. Fig. 1 shows a snapshot of the molecular dynamics (MD) simulation, in which the system domain consisted of a cubic cell. The length was varied in the range of 5.65–5.67 nm, resulting in a volume of 180.36–182.28 nm^3. The system filled with 3000 water and 870 EG molecules, as a base fluid, with a mass ratio of 1:1 (volume ratio of 1:1.1). A graphene sheet containing functional groups, with a dimension of about 0.7 nm when stretched, was added to perform the simulation, which has 21 hydrogen atoms at the edge to allow for modification by functional groups (see Fig. 2). We fixed the dimensions of the cell, and systematically varied the number of functional groups from 2 to 21 in order to quantitatively assess the effect of affinity. The functional groups employed in this study were alkanol and alkanol amine, produced via Hummer's method [34].

Second, we evaluated the size effect of the graphene sheet using a cubic cell with fixed sides containing a single graphene with various sizes. The size can be described by several representative factors, such as the length of the sides, the number of carbon atoms, and the number of sp^2-hybridized carbon atoms (benzene-ring). We used the number of carbon atoms assuming that the graphene sheets are mostly square-like; they ranged from 24 to 482 carbon atoms, corresponding to 0.815–4.0 nm of the graphene sheet on one side. In addition, each sized-graphene sheet was used to investigate the effect of functional groups using three types of graphene sheet (with 4, 8, and no functional groups). The functional groups were determined arbitrarily considering their symmetric degrees of freedom for the motion preventing interference from other functional groups [29].

All carbon atoms consisting of graphene are sp^2-hybridized bonds. The simulations used Verlet velocity algorithm for the integrating the equations of the motion [35], and were performed at room temperature (298 K), which was set using the Nose-Hoover-Langevin (NHL) thermostat [36,37], and the *NVT* ensemble method with a 1 fs time step (where N is the number of atoms, V is volume, and T is the temperature). The total time of each simulation was 1 ns, which reached a stable state.

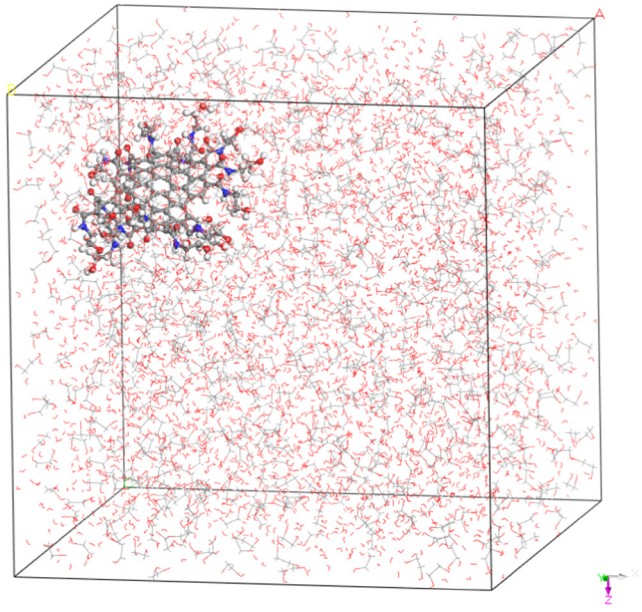

Fig. 1. Snapshot of a molecular dynamics (MD) simulation of nanofluid containing graphene with functional groups.