Percolation theory at work – boosting the heat transfer performance of graphitic nanofluids

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ABSTRACT

We have investigated the effects of nanoparticle morphology, surface treatment and concentration on the thermo-physical properties of nanofluids with graphitic nanomaterials in EG/H_2O base fluid. The particle morphology along with surface treatment and concentration needs to be considered in formulation of graphitic nanofluids to achieve advanced heat transfer coefficients. Adjusting the nanoparticle concentration to the percolation threshold allows closing the gap between high thermal conductivity, viscosity and advanced heat transfer in graphitic nanofluids.

The implementation of this technology in HEV's and EV's will result in reducing the size, weight and number of heat exchangers and improving overall vehicle efficiency.

Keywords: nanofluid, graphite nanosheets, percolation, heat transfer, viscosity

1 NANOFLUID ENGINEERING

In the area of heat transfer fluids, nanofluids refer to the engineered suspensions of nanometer-sized (less than 100 nm in at least one dimention) solid particles in conventional heat transfer fluids to enhance the thermal conductivity and the heat transfer coefficient. Nanoparticles are typically made of chemically stable metals, metal oxides or carbon. Some combinations of nanoparticles and liquids have been shown to substantially increase the heat transfer characteristics of the nanofluid over the base liquid [1].

A plethora of studies have reported high thermal conductivity of nanofluids with high aspect ratio carbon nanoparticles such as graphenes and carbon nanotubes [2, 3]. Although many report thermal conductivity enhancements in carbonaceous nanofluids there is no agreement on the concentration effect of such nanomaterial additives.

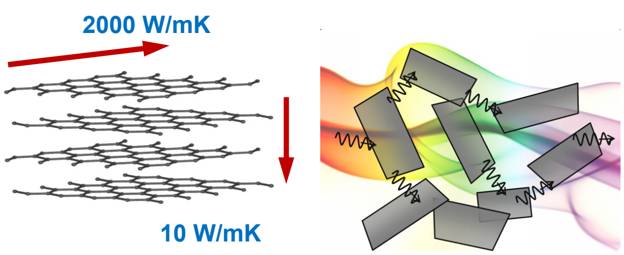

Figure 1. Schematics of (left) thermal conductivities in anizotropic carbon nanoparticles and (right) percolation in nanofluid with graphite nanosheets.

Some carbon nanomaterials have anisotropic thermal conductivity (Figure 1 left) and can engage several heat transfer mechanisms in suspensions e.g. effective medium theory, percolation, and plasmon resonances.

In this study we have investigated different grades of multilayer graphene nanoplates (xGnPs). These nanoparticles can be described as multilayered graphene nanoplatelets or nanothin graphite chips with various diameters and thicknesses. The multilayered GnPs have anistropic thermal conductivity with ~ 2000 W/mK along the hexagonal carbon layers and only ~ 10W/mK perpendicular to the layered graphite structure. The advantage of such materials is that they are commercially available in large scale at low cost in a variety if sizes and thicknesses. This allowed us to study the effect of particle morphology and surface treatment on the resulting nanofluid properties.

2 PERCOLATION THEORY

In systems like carbon nanotube, graphite and graphene oxide nanofluids the nanoparticle percolation networks can be formed (Figure 1 right), which along with high anisotropic thermal conductivity of those materials result in abnormally increased thermal conductivities up to 100-200% increases in thermal conductivity.

Such dramatic increases in thermal conductivity of nanofluids are most likely due to the unique nature of highly anisotropic carbon nanomaterials that allows engaging multiple heat transfer mechanisms in suspensions (arising from the effective medium theory, percolation, and plasmon resonances). The drawback of carbon nanofluids with high aspect ratio particles is very high viscosity (up to 3 orders of magnitude higher than viscosity of the base fluid). Elongated particles and agglomerates also result in higher viscosity than spheres at the same volume concentration, which is due to structural limitation of rotational and transitional motion in flow [5, 6]. Therefore spherical particles or low aspect ratio spheroids are more practical for achieving low viscosities in nanofluids – the property that is highly desirable for minimizing the pumping power penalties in cooling system applications.

Such viscosity increases result in pumping power penalties that are much higher than the benefits in thermal conductivity of suspensions. Thus, the practical value of previously reported carbonaceous nanofluids is not sufficient for commercialization of the technology. In development of nanofluids for heat transfer a fine balance needs to be obtained between increases in thermal conductivity and viscosity. For graphitic nanoparticle suspensions, advanced thermal conductivity is observed

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when nanoparticle percolation threshold is achieved. The concentration of the percolation threshold will vary with particle morphology, and both platelet diameter and thickness are important for that matter. Besides the important role of surface charges in nanoparticle agglomeration and viscosity of nanofluids, particle shape effect can also play a role in abnormally increased viscosity of graphitic nanofluids. Shear rate dependence of viscosity in suspensions indicates some restriction in fluid movement due to particle alignment and/or agglomeration. In a steady state, a rod-like particle or elongated agglomerate can have two types of motion due to the Brownian movements: rotational (end-over-end) motion around the mid-point, and translational motion in parallel or perpendicular to the long axis. When the average spacing between particles is much larger than the longest dimension of the particle, the rotational and translational motions are not restricted by each other; hence very weak shear thinning behavior is expected. In suspensions of different grades of GnP nanoplatelets particle radius (R) and thickness (L) are varied. To provide free rotational movement to the nanopalatelets each nanoparticle has to be suspended in a spherical volume proportional to the longest particle dimension $V_{rot}=4/3*\pi*R^3$, while the volume of platelet shaped nanoparticle is $V_{np}= \pi*R^2*L$, thus volume fraction of nanoparticles (ϕ) to achieve the percolation threshold can be calculated as $\phi=V_{np}/V_{rot}=3/4*(L/R)$.

3 PARTICLE MORPHOLOGY

Graphite nanoplatelets (GnP) used in this study varied in thickness as ~ 2 nm (A-GnP), 6 nm (B-GnP) and 12 nm (C-GnO) and surface areas of 750 m^2/g, 120-150 m^2/g and 60-80 m^2/g, respectively as received from XGSciences Inc. Electron microscopy images of as-received GnP powders are shown in Figures 2a – 2c. The difference in platelet thickness is not obvious from the image resolution, but there is a clear difference in platelet diameters. All GnP nanoparticles have irregular shape with particle diameters varying from 0.1-1 microns in A-GnP, from 1-10 microns in B-GnP and 3-25 microns in C-GnP grade.

4 SURFACE MODIFICATION

GnP manufacturing processes are non-oxidizing, thus producing a pristine graphitic surface of sp^2 carbon molecules with minor oxidation at edges. Thus, as received GnP nanomaterials are highly hydrophobic, i.e., suspensions of gnps in water and water/ethylene glycol mixtures require use of surfactants.

As received GnP graphitic nanopowders have very poor suspension stability in water, especially at low concentrations. The manufacturer suggests using a surfactant to improve dispersions of graphitic nanopowders in aqueous solutions. A series of tests were conducted that investigated the effect of cationic and anionic surfactants on thermal conductivity and stability of suspensions with A-GnP nanoparticles in deionized water.

An alternative way of getting stable dispersions of graphitic nanoparticles by surface modification of carbon surfaces with hydrophilic groups was also tested and resulting nanofluids were compared to the suspensions stabilized with surfactants. To achieve stable suspensions of GnP in EG/H_2O base fluids use of surface functionalization/oxidation of sp2 graphite platelets was found the most efficient with least effect on thermal conductivity. Functionalized GnP (F-GnP) after treatment of nanoparticles in 3:1 mixture of concentrated H_2SO_4 and HNO_3 show change of morphology and surface chemistry observed with SEM and Raman spectroscopy.

Suspensions with unmodified GnPs settle within a few hours, but initial reading of thermal conductivity show enhancements slightly above the effective medium theory predictions. Suspensions stabilized with cationic (CTAB) or anionic (SDS) surfactants show similar improvement in stability; however, thermal conductivity of those suspensions is below the base fluid due to very low thermal conductivity of organic molecules compared to water. In addition, segregation of surfactants at liquid/nanoparticle interface creates additional thermal resistance for heat flow. Thus organic surfactants are detrimental for the thermal conductivity of water-based suspensions. Use on non-surfactant approach to stabilizing dispersions of nanoparticles involves an additional surface functionalization step as described hereinafter. The resulting dispersion of F-A-GnP nanoparticles in water has superior stability even compared to suspensions stabilized by surfactants, and also showed improved thermal conductivity values. The SEM images of Figures 2b – 2d show that a surfactant only slightly breaks granular agglomerated nanoplatelets, while surface functionalization clearly separates GnPs to individual nanoplatelets. Therefore, the surface functionalization method was a highly preferred method for preparing stable nanofluids from all grades of GnP nanoparticles.Surface functionalization increases surface concentration of hydroxyl and carboxylic groups and charges, engaging electrostatic stabilization. Graphitic core/ graphene oxide shell nanoplatelets produce high stability suspension in water and provide percolation paths for heat conduction.

The morphology of the GnP nanoparticles before and after functionalization can be considered by comparison of various SEM images. As-received GnPs assemble into compact clusters on a Si wafer surface, especially A-GnP grade, which is indicative of the hydrophobic nature of platelets.

SEM images of a comparison of as received and f-GnPs (see Figures 2d-2f) show a dramatic change in morphological appearance of nanoparticles before and after the functionalization process. The F-GnPs are very well distributed on the surface of Si wafer with individual nanoplatelets lying flat, compared to granular agglomeration and clustering of unmodified nanoparticles depicted on Figure 2a-2c. This is a clear sign of the hydrophilic nature of the nanoparticle surface that also helps in stabilization of f-GnP suspensions.

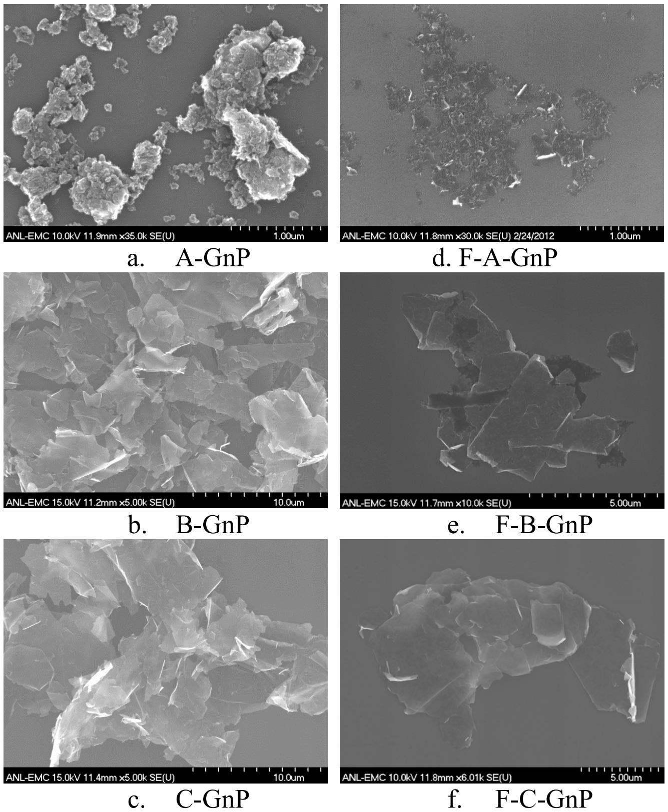

Figure 2. Scanning electron microscopy of three grades of (a-c) graphite nanosheets as received and (d-f) corresponding material after surface treatment.

Surface functionalization is believed to convert oxidized sp^2 graphitic layers into a variety of hydroxy- and carboxylic ionic groups. These groups can carry electrostatic charge and are miscible with water based fluids. Thus, core-shell structures of graphitic gore and graphene oxide shell are formed. On one hand, surface oxidation helps increasing the stability and decreasing viscosity of nanofluids; but, on the other hand, thermal conductivity of graphene oxides is much smaller than that of graphite and graphene. Therefore, the functionalization process decreases enhancements in thermal conductivity due to formation of surface oxides.

5 HEAT TRANSFER

Nanofluid heat transfer is a relatively new field and has been focused on determining the levels of potential thermal conductivity and heat transfer enhancement of a variety of nanofluids. In these investigations, the emphasis was usually on the magnitude of the thermal phenomena and not on the viability of the fluids for commercial applications. One particular area of application for nanofluids is in the field of power electronics, which is a critical component of hybrid electronic vehicles (HEVs) and electric vehicles (EVs) since it provides control and conversion of electric power. Increasing power loads result in increased heat fluxes, thus uninterrupted operation of power electronics requires liquid cooling systems to enhance heat dissipation, improve energy efficiency, and lengthen device lifetime. In current hybrid electric vehicles, two cooling systems are used: a higher temperature system for cooling the gasoline engine and a lower temperature system for cooling the power electronics. An important commercial goal is to eliminate the lower temperature system and to accomplish all cooling with a single higher temperature system. This would obviously reduce weight (thereby increasing fuel economy) and also reduce complexities.

In recent work a heat transfer analysis for a typical heat exchanger has been performed to determine the magnitude for enhancement in the thermal properties of a heat transfer fluid required to improve the cooling. Calculations have shown that for a designated heat exchanger (laminar flow) that an enhancement in thermal conductivity of between 50% and 100% could, without a significant increase in pumping power, allow either elimination of one radiator in HEVs or an increase in the loading. To satisfy these thermal management needs, the heat transfer efficiency of conventional fluids must be improved.

At nanoparticle loadings of 5 wt. % the thermal conductivity of F-B-GnP and F-C-GnP was 75% and 80% correspondingly (not shown here), however viscosity of F-C-GnP suspension was more than 100 times higher than F-B-GnP nanofluid.

As noted earlier, in suspensions of nanoplatelets with higher than critical volume fractions nanoparticles start to interact, so the viscosities at zero shear rate can be much greater than the base fluid viscosity and be very sensitive to the shear. At concentrations of nanomaterials that are significantly above the percolation threshold, an extended microstructure is created in a nanofluid, obstructing the fluid flow and producing high viscosities. Because of high polydispersity of GnP powders the average particle diameter should be evaluated with additional methods, since difference in critical particle concentration is strongly dependent on the diameter. Experimental evaluation of the percolation threshold through viscosity/thermal conductivity measurements is also a possible approach.

Since the cooling efficiency of the heat transfer fluids is the main consideration in the current nanofluid development, the ratio of heat transfer coefficients for the suspensions and the base fluid was estimated for fully developed (hydrodynamically and thermally), laminar and turbulent flow regimes using conventional fluid dynamic equations. The ratio of heat transfer coefficients is a convenient measure for comparison of two fluids flowing in the same geometry and at the same flow rates. In a laminar flow regime, the heat transfer coefficients are proportional to the thermal conductivity (within the acceptable range of inlet/outlet temperature difference), but in a turbulent flow regime the heat transfer coefficients depend on a set of thermo-physical properties. Introduction of nanoparticles to the fluids changes density (ρ), thermal conductivity (k)

viscosity (μ), and specific heat (Cp) of the coolant. In the case of hydrodynamically and thermally fully developed laminar flow, the heat transfer coefficient (h) is proportional to the thermal conductivity (k), and within the acceptable range of inlet/outlet temperature difference is independent of the flow velocity:

$$\frac{h_{nf}}{h_0} \approx \frac{k_{nf}}{k_0} \quad (1).$$

The comparison of two liquid coolants flowing in fully developed turbulent flow regime over or through a given geometry at a fixed velocity reduces to the ratio of changes in the thermo-physical properties:

$$\frac{h_{nf}}{h_0} \approx \left(\frac{\rho_{nf}}{\rho_0}\right)^{4/5} \left(\frac{c_{p\,nf}}{c_{p\,0}}\right)^{2/5} \left(\frac{\mu_{nf}}{\mu_0}\right)^{-2/5} \left(\frac{k_{nf}}{k_0}\right)^{3/5} \quad (2).$$

The nanofluid is beneficial when h_{nf}/h_0 ratio is above one and not beneficial when it is below one.

Experimental values for thermal conductivity and viscosity (density and specific heat were calculated from the rule of mixtures) were used for evaluation of heat transfer benefits of nanofluid with 5 wt.% of F-B-GnP (Figure 3). The ratio of heat transfer coefficients (h_{nf}/h_0) for the nanofluid (h_{nf}) and the base fluid (h_0), calculated for different temperatures, shows that the inclusion of graphitic nanoparticles in EG/H_2O coolant can provide significant 75-90% improvement in heat transfer rates when used in laminar flow regime, improving with increase in temperature. Heat transfer coefficients in the turbulent flow regime show 30-40% improvement in heat transfer compared to the base fluid. Previously it was observed that the heat transfer coefficient improves with temperature for nanofluids in both water based and organic base fluids. These results are very advantageous, since the enhancements levels not only meet the power electronics cooling criteria, but also will be beneficial in thermal management in medical, transportation, military, and many other applications.

6 SUMMARY

Morphology and surface functionalization of graphitic nanoparticles have been developed for advantageous, improved thermo-physical properties and heat transfer performance of nanofluids in EG/H_2O base fluid. Suspensions with larger diameter and thickness of nanoparticles provide the highest increase in thermal conductivity, however, viscosity increase of ~100 times makes this fluid impractical for heat transfer applications. The optimization of viscosity and thermal conductivity increases in nanofluids is required for development of practical nanofluid with advanced heat transfer.

Surface functionalization of GnP powders created core/shell graphite/graphene oxide nanoplatelets that form stable suspensions in water based fluids. The optimization of nanoparticle surface chemistry and selection of particle morphology allowed producing nanofluid that meets the property criteria for efficient power electronics coolant, as well as other applications requiring such advantageous properties.

Formulation of an efficient nanofluid for heat transfer can include adjusting nanoparticle concentration for given morphology of nanoparticles to reach the percolation threshold, but to minimize the obstruction to fluid flow. A balance was achieved with an example B-GnP grade of functionalized nanomaterials. Simple, low cost, and up-scalable surface modification methods are quite achievable for graphitic nanoparticles formulated in accordance with the invention; and the nanofluid coolant was obtained with an advanced combination of properties that allows 75+% improvements in heat transfer coefficient when used in laminar flow and 30+% enhancements in heat transfer coefficient when used in turbulent flow. The implementation of this technology in HEV's and EV's will result in reducing the size, weight and number of heat exchangers, further improving vehicle efficiency and fuel economy.

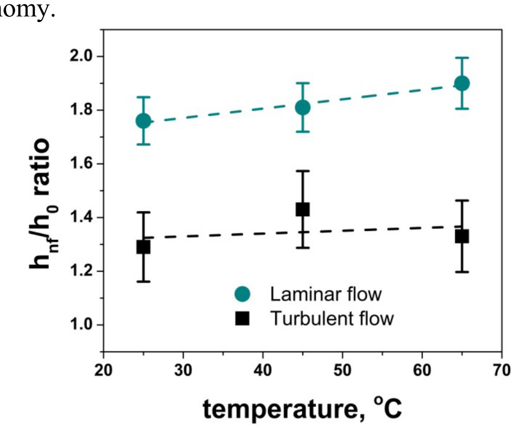

Figure 3. Ratio of heat transfer coefficients for graphitic nanofluid and EG/H_2O base fluid in laminar and turbulent flow regimes.

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REFERENCES

[1] Timofeeva E., et. al., Nanoscale Res. Lett., 2011.6: p. 182.

[2] Yu, W., et al., Phys. Lett. A, 2011. 375(10): p. 1323-1328.

[3]Yu, W. et al. , J. of Nanofluids, 2013. 2:p. 69–73.

[4] Zhu, H.T., et al., Carbon, 2007. 45(1): p. 226-228.

[5] Yang, Y., et al., J of Nanoscience and Nanotechnology, 2005. 5: p. 571-579.