

NANOCARBON NANOFUIDS: COMPARISONS BETWEEN MORPHOLOGY AND NANOSTRUCTURE

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ABSTRACT

Reported here are experimental results of studies designed to identify the operable mechanisms responsible for the gains in thermal conductivity of nanofluids based on nanocarbons. Comparison of functionalized versus nonfunctionalized nanocarbons addresses the effect of interfacial fluid ordering. Comparison between graphitized and nongraphitized carbon black addresses the effect of long-range phonon propagation. Comparison between MWNTs and carbon black addresses particle aggregation by comparing two very different, yet fixed, nanocarbon morphologies. Lastly partial network formation, i.e., spatially distributed clustering is addressed by varying concentrations with the different nanocarbon morphologies.

Keywords: nanofluids, nanocarbon

1 INTRODUCTION

Nanofluids have received great attention given reported gains in thermal conductivity. Yet the origin of these gains is highly debated. Critical comparisons are often lacking within a given study. Comparison between studies introduces the attendant problem of different nanoadditives, concentrations, particle structure, potential or unknown aggregation, and surface chemistry [1]. In general nanofluids contain organic or inorganic particles ranging in size from 10's to 100's of nanometers. With the burgeoning growth of nanomaterials, the number of formulations is nearly infinite. Unfortunately as more nanofluids are tested for enhanced thermal conductivity, the range of values is also expanding. Therein comparison between proposed mechanisms was investigated here..

2 EXPERIMENTAL

Experimental details will be presented at the presentation with regards to the synthesis and utilization of the nanomaterials. Further details may be found elsewhere [1].

3 RESULTS AND DISCUSSION

Table 1 summarizes the nanofluids and their thermal conductivity as a percentage increase relative to that of the

base fluid, water. Different patterns correspond to different mechanistic tests of a particular value. Characterization of surface chemistry was performed by XPS for both nascent and functionalized nanocarbons. The concentration of surface oxygen functional groups increased by ~20% for the various nanocarbons. As described, the dispersal agent, the surfactant, was used with all nanoadditives. Suspensions remained stable for weeks. Therein effects due to varying degrees of dispersion are ruled out as a causative factor in the observed thermal conductivity. (Aggregates would only grow with time and result in flocculation and/or precipitation). Results for each of the remaining comparative tests; long-range phonon transport, interfacial ordering, particle clustering, and partial network formation are examined next.

3.1 Baseline Results

The thermal conductivity increase for the nascent carbon black is 5.6% and for the MWNT is 4.6% relative to that of water. Comparative testing with only the surfactant yielded an increase of <1% enhancement, deemed as within measurement uncertainty. Therein the observed increases are attributed solely to the nanocarbon additive.

3.2 Interfacial Ordering

Figure 1 shows the comparisons between the different nanocarbons, used to formulate the nanofluids. With reference to values listed in Table 1, functionalization of the MWNTs increases knf by nearly 400% relative to the nonfunctionalized form. Similar dramatic increases in knf are found for CB-G and R-250 upon functionalization where knf increases by the ratios 19/8 and 17/5.6 respectively (referring to percentage increases listed in Table 1). Such gains clearly point to the dramatic influence of interfacial molecular structure upon the interfacial thermal resistance. Polar oxygen groups such as C = O, C-OH and COOH are introduced using the HNO₃/H₂SO₄ treatment [13]. Such groups would be expected to hydrogen bond with water and facilitate formation of an ordered solvation shell. Such molecular order coupled with the covalent attachment of the ligands to the carbon particle would be expected to enhance phonon coupling between the liquid and solid phases. Such impedance matching is fundamental to thermal wave (phonon) transmission.

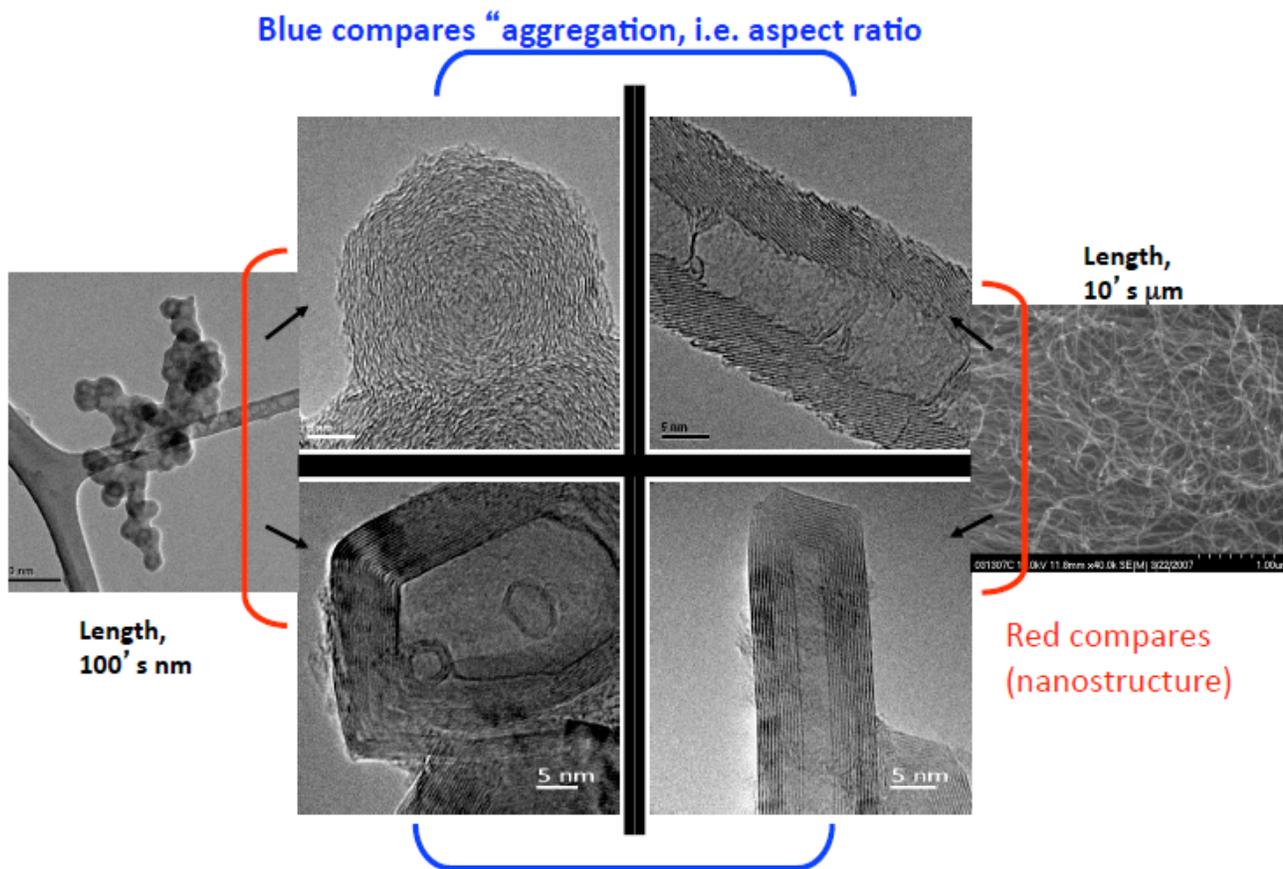


Figure 1 - Four nanocarbons were studied in order to facilitate the cross comparisons for the different mechanisms. Comparisons between graphitized and non-graphitized forms of either spherical (0D) or nanotubes (1D) enabled comparisons of the influence of solid-state structure. Different morphologies of the same solid-state structure (i.e. disordered versus graphitic) enables comparison between shapes.

Nanocarbon	Nascent – Non-functionalized	Functionalized – (-OH, C=O, COOH)
Carbon Black	5.6	17
Nano-onions	8.0	19
Carbon Nanotubes	4.6	16

Table 1 – Summary of thermal conductivity gain (%) relative to the base fluid, water, for the listed nanocarbons, each at an added weight percent of 0.5%. These polar groups would also be expected to displace the surfactant.

As polar groups capable of H-bonding, the oxygen moieties themselves would act as a surfactant given favorable energetics for interaction with solvent water molecules. Moreover their hydrophilic nature would preclude interaction with the hydrophobic end of the surfactant. If functionalization did not displace surfactant to create a stronger interaction with the near-surface solvent, then k would have remained constant instead of increasing. Interfacial molecular ordering is clearly a significant contribution to nanofluid thermal conductivity.

An interesting related parameter is accessible surface area. Despite differences in absolute lengths and aspect ratios, the two nanocarbons (MWNTs and CB) have similar exposed perimeter surface areas, ~ 50 m²/g [16]. With interfacial resistance as a dominant factor, as noted previously, then a corollary is that interfacial resistance is inversely proportional to accessible surface area. Implicitly understood is that “available surface area” pertains only to exterior surface as only those surfaces that can interact with

the solvent and form an ordered interfacial layer will contribute to thermal conductivity enhancement. Despite the compact nature of the fractal aggregates, the primary particle substructure substantially increases the exposed surface area, resulting in similar surface areas for the MWNTs and CB.

Gains in nanofluid thermal conductivity have been attributed to interfacial fluid ordering, long-range phonon transport and particle aggregation. Through comparisons between nascent and functionalized nanocarbons, interfacial (molecular) ordering was shown to be the major factor responsible for thermal conductivity enhancement. This is applicable for both elongated MWNTs and compact carbon black aggregates. Comparisons between graphitized and nongraphitized carbon black revealed a relatively small enhancement to knf by internal phonon transport. This applied for both functionalized and nonfunctionalized forms. The similar nanostructure of MWNTs and carbon black allowed comparisons between these two different nanocarbons with very different morphologies. Different morphologies permits surrogate testing of particle clustering while maintaining identical concentrations and dispersions. For the same concentration these two different nanocarbons exhibited nearly identical thermal conductivities. Although functionalized forms of each carbon had substantially higher nanofluid thermal conductivities than their nonfunctionalized (nascent) counterpart forms, nearly identical values were observed for MWNTs and carbon black as additives at two different concentrations. This comparison between the two morphologies and different concentrations suggests an additional contribution to the thermal conductivity.

Dispersion of each material is important to achieving maximum enhancement for a given additive amount. Well before establishment of a percolation threshold, partial networks can form. Distinct from aggregation forming compact assemblies, clustering results in spatially distributed partial “networks” consisting of a few contacting nanoparticles. Functionalization may aid the formation of such networks through hydrogen bonding. Such interparticle connections eliminate fluid-nanoparticle junctions and associated resistances while establishing instead particle-particle connections. The phonon transport through the solid-solid connection is expected to be much more facile given matched phonon frequencies between the CNTs. As a result, nanoadditive concentrations below the percolation threshold can offer substantial gains in thermal conductivity via this mechanism. Given that solid-state phonon transport as governed by nanoparticle nanostructure is not significant, the operative physical factor by which partial networking enhances thermal conductivity is reduction of interfacial resistance. Correspondingly higher concentrations are less effective as proportionally fewer nanoparticle-fluid interfaces are eliminated (in favor of more solid-solid connections). Establishment of extended networks (clusters), ultimately reaching a percolation network may impose a practical limit on the nanocarbon

additive concentration given fluid viscosity constraints of practical cooling systems.

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REFERENCES

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