An innovative studies and analysis on thermal behavior in nanofluids

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Abstract

Nanofluids are dilute liquid suspensions of nanoparticulate solids including particles, nanofibers and nanotubes. Such materials were first brought into attention approximately a decade ago when enhanced thermal behavior was observed. A sizable community has now formed, which starts to generate a critical mass in the area. Nanofluids are fluids containing nanosized particles, have superior heat transfer properties, e.g. heat transfer and thermal conductivities. Publications on nanofluids are increasing exponentially in the past few years covering theoretical, experimental and numerical aspects of formulation, characterization, flow behavior and thermal behavior of nanofluids. The focus of the present work concerns that the thermal properties of suspensions of nanoparticles in fluids, commonly referred to as nanofluids. Investigations of their thermal properties have thrown up many findings that are interesting and challenging to describe. The importance of thermal properties is in the context of heat removal from small spaces. It is a technological challenge arising from the need to cool high-speed micro-electronic devices, and also, they have been recommended as a promising option for various engineering applications, due to the improvement in the effectiveness of thermal phenomena. The purpose of this paper focuses on the importance of thermal properties, different techniques for measuring the thermal conductivity, thermal phenomena in nanofluids, especially the new application trends for nanofluids in addition to the heat transfer properties of nanofluids. And also this article will be used for researchers on nanofluids.

Keywords and Pacs

Heat transfer - convective, 44.25.+f, 44.27.+g
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Magnetic fluids, 47.65.Cb
Thermal diffusivity, 66.30.Xj
Thermal properties - of nanocrystals, and nanotubes 65.80.-g
Thermal instruments and apparatus, 07.20.-n
Viscosity, diffusion, and thermal conductivity, 51.20.+d

Theoretical Models

A number of studies have been reported in the recent past, on the heat transfer characteristics of suspensions of particulate solids in liquids, which are expected to be cooling fluids of enhanced capabilities, due to the much higher thermal conductivities of the suspended solid particles, compared to the base liquids. However, most of the earlier studies were focused on suspensions of millimeter or micron sized particles, which, although showed some enhancement in the cooling behavior, also exhibited problems such as sedimentation and clogging. The gravity of these problems has been more significant in systems using mini or micro-channels.

Nanofluids have been searched to possess enhanced thermophysical properties such as thermal conductivity, thermal diffusivity, and convective heat transfer coefficients compared to those of base fluids like oil or water. It has demonstrated great potential applications in many fields. A much more recent introduction into the domain of enhanced-property cooling fluids has been that of nanoparticle suspensions or nanofluids. Advances in nanotechnology have made it possible to synthesize particles in the size range of a few nanometers. These particles when suspended in common heat transfer fluids, produce the new category of fluids termed nanofluids. The observed advantages of nanofluids over heat transfer fluids with micron sized particles include better stability and lower penalty on pressure drop, along with reduced pipe wall abrasion, on top of higher effective thermal conductivity.

Quantitative analysis of the heat transfer capabilities of
nanofluids based on experimental methods has been a topic of current interest. The present article attempts to review the various experimental techniques used to quantify the thermal conductivity, as well as to investigate the thermal phenomena in nanofluids and the applications of nanofluids.

Increase in thermal conductivity depends on nanoparticle material, size and concentration. Nanoparticles have a large surface area-to-volume ratio; a 1 nm spherical particle has a surface area-to-volume ratio 1000 times greater than that of a 1 m particle; Kapitza resistance becomes important for such large surface areas. Increase in thermal conductivity is beyond the classic Maxwellian model predictions. Literature survey reveals that there are large number of models for estimating thermal conductivity of nanofluids.

The existing models can be categorised into two general groups:

(i) Static models which assume stationary nanoparticles in the base fluid in which the thermal conductivity is predicted by conduction-based models such as Maxwell12, Hamilton- Crosser13, and others14,15, using conductivity of phase constituents and volume fractions,

(ii) Dynamic models based on random motion of the nanoparticles in fluid (Brownian motion) and responsible for transporting energy through collision between nanoparticles or micro liquid convection, mixing that enhances the transport of thermal energy.

Modelling of nanofluid properties has been done through molecular diffusion simulation. Some of the basic models used to estimate the thermal conductivity based on above two approaches are shown in Table below. Heat transfer coefficient increase are on top of the thermal conductivity. Possible mechanisms considered for this increase are nanoparticle diffusion and boundary layer thinning, dispersion and enhanced turbulence. Increase in critical heat flux may be attributed to alteration of nucleation site by nanoparticle. Simultaneous studies of thermal conductivity and viscosity may give additional insight into enhanced heat transfer. Surface modification or functionalisation may also lead to stronger thermal conductivity enhancements.

Table 1. Nanofluids with their thermal conductivity, increase in nanofluid thermal conductivity over base fluid thermal conductivity and synthesis procedure used as reported in the literature

<table>
<thead>
<tr>
<th>Base fluid with conductivity</th>
<th>Nano particles, average diameter and concentration</th>
<th>Method used for synthesis</th>
<th>Max. thermal conductivity ratio</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water 0.613</td>
<td>Al₂O₃, &lt;50 nm, up to 4.3 vol%</td>
<td>2-step</td>
<td>1.08</td>
<td>[1]</td>
</tr>
<tr>
<td>Water 0.613</td>
<td>TiO₂, 15 nm, &lt;5.0 vol %</td>
<td>2-step</td>
<td>1.30</td>
<td>[2]</td>
</tr>
<tr>
<td>Cirate</td>
<td>Ag, 6-80 nm, 0.1 vol %</td>
<td>2-step</td>
<td>1.85</td>
<td>[3]</td>
</tr>
<tr>
<td>α-Olephin</td>
<td>CNT, 25x50000 nm, 1.0 vol%</td>
<td>2-step</td>
<td>2.50</td>
<td>[4]</td>
</tr>
<tr>
<td>Thiolate</td>
<td>Au, 10-20 nm, 0.1 vol %</td>
<td>2-step</td>
<td>1.09</td>
<td>[3]</td>
</tr>
<tr>
<td>EG 0.252</td>
<td>Al₂O₃, &lt;50 nm, up to 5.0 vol%</td>
<td>2-step</td>
<td>1.18</td>
<td>[1]</td>
</tr>
<tr>
<td>EG 0.252</td>
<td>Cu 10 nm, up to 0.5 vol%</td>
<td>1-step</td>
<td>1.41</td>
<td>[5]</td>
</tr>
<tr>
<td>Water 0.613</td>
<td>Cu, 75-100 nm, 1.0 vol %</td>
<td>1-step</td>
<td>1.23</td>
<td>[6]</td>
</tr>
<tr>
<td>Water 0.613</td>
<td>Cu, 18 nm, up to 5.0 vol%</td>
<td>1-step</td>
<td>1.60</td>
<td>[7, 6]</td>
</tr>
<tr>
<td>Water 0.613</td>
<td>C-MWNT 50 nm, 5 um 3 urn, 0.6 vol%</td>
<td>2-step</td>
<td>1.38</td>
<td>[8]</td>
</tr>
<tr>
<td>Oil (Trans.) 0.145</td>
<td>Cu, up to 100 nm, up to 7.6 vol%</td>
<td>2-step</td>
<td>1.43</td>
<td>[7]</td>
</tr>
</tbody>
</table>
Thermal characterisation of Nanofluids

Choi1 established the field of nanofluids1 in 1995, and in 2001 measured thermal conductivity enhancement of 160 per cent for MWCNT’s dispersed in poly (a-olefin) oil. Several groups have measured thermal conductivities far in excess to those predicted by the Maxwell model, while it has been hypothesised that small particle size, and hence large surface area is important. Research conducted on copper oxide nanoparticles by two different groups reported that the nanofluid containing larger particles exhibited higher thermal conductivity. Das18 et al. reported that nanofluids exhibit a strong dependence on temperature, with a correlation between higher conductivities and higher temperatures. The uniqueness of nanoparticles and nanofluids is that no current model, applicable to larger particles, can estimate the enhancement of nanoparticles because of the breakdown at continuum at the nano size.

Measurement of Thermal Conductivity of Nanofluids

There are steady state and transient methods for the measurement of thermal properties. Although steady-state methods are simple theoretically, these involve rather elaborate technique practically, including thermal guard to eliminate lateral heat flow and electronic control system to enable stable condition during the test. Transient methods provide fast measurement and reduce unwanted modes of heat transfer. Most thermal property measurements of nanofluids have been done using transient method of measurement. The measurement of thermal diffusivity and thermal conductivity is based on the energy equation for conduction.

The thermal conductivity of nanofluid has been measured using the transient hot-wire method where the temperature increase of the platinum wire (referred as hot-wire) is related to the thermal conductivity K_{eff} of the fluid30, widely employed to measure thermal conductivity of nanofluids31,32. Modified form of hot wire method referred as transient thermal probe method33,34 is being used by the author to measure the thermal conductivity of nanofluids.

Zhang34, Zhang35 et al. have used transient short hot wire method to simultaneously measure thermal conductivity and thermal diffusivity of Au/toluene, Al_{2}O_{3}/H_{2}O, carbon nano fibre/H_{2}O36 and ZrO_{2}/H_{2}O, TiO_{2}/H_{2}O CuO/H_{2}O36. Murshed37 et al. have used double hot wire method to measure thermal diffusivity of nanofluids. Literature reported thermal conductivity for various nanofluids containing spherical or cylindrical solid particles is shown in Table 1.

Recently scanning thermal conductivity microscope (trade name Scanning Thermal Microscopy SThM) has been developed38 to meet the need for thermally imaging devices and nanostructures. It aimed to directly measure thermal conductivity of microscopic structures and features such as fibres, fibre coatings, grain boundaries, grains and intergranular phases.

While the spatial resolution of other thermometry techniques based on far-field optics are diffractionlimited to the order of several microns, spatial resolution of 50 nm has been demonstrated for SThM.

SThM operates by raster scanning having a sharp temperature sensing tip on a solid surface. The temperature-sensing tip is usually mounted on a micro cantilever of an atomic force microscope (AFM) probe so that tip-sample constant contact force is maintained by the force feedback loop of the AFM.

While the tip scans a sample, tip-sample heat transfer changes the tip temperature, which is measured and used to calculate the temperature or thermal properties of the sample at the tip-sample contact. This information in combination with probe position is used to construct a digital gray scale image of the surface with sub-micron resolution. SThM has been used to locate hot spots in electronic devices and to image contrast in thermal properties of composite thin film materials.

Observations made from literature reviews are as follows:

Thermal conductivity is enhanced by 30 per cent for Al_{2}O_{3} water suspension at a volume of 4.3 per cent. In case of Cu-water nanofluid the thermal conductivity enhancement is 17 per cent for 4 per cent nanoparticle volume fraction. Enhancement in thermal conductivity of CuO ethylene glycol nanofluid is 4 per cent and 22 per cent, respectively, for nanoparticle volume fraction of 1 per cent and 5 per cent. In case of CNT in ethylene glycol increase in thermal conductivity is 12.4 per cent for 1 per cent volume and in synthetic oil increase is 30 per cent for a volume of 2 per cent.

Thermal conductivity increase is 11.3 per cent for MWCNT in water for 1 per cent volume fraction. Increase in thermal conductivity is 4 per cent for SiO_{2}-water nanofluid having 1 per cent nanoparticles by volume fraction. The experimental studies on thermal conductivity with temperature using transient hot probe method for Ag, Fe and S for nanofluids being carried out by the author also indicate about 30-40 per cent increase in thermal conductivity for Ag and Fe nanofluids. A number of possible reasons for this behaviour have been proposed1. Several authors10,11 have argued that large thermal conductivity increase is due to hydrodynamic effect of Brownian motion of nanoparticles.

Keblinski9 et al. put across four possible explanations for the increase, i.e., Brownian motion of particles, molecular level layering of the liquid at liquid-particle interface, nature of heat transport in nanoparticles and effect of nanoparticle clustering. Particle aggregation and the formation of extended structures of linked nanoparticles may be responsible for much of the disagreement between experimental results and the predictions of effective medium theory.
Simultaneous studies of thermal conductivity and viscosity may give additional insight into enhanced heat transfer. Surface modification or functionalisation may also lead to stronger thermal conductivity enhancements.

Table 2. Basic thermal conductivity models, where \( K_{\text{eff}} \) is the effective thermal conductivity of solidfluid mixture, \( a = K_2/K_m \), \( K_m \) and \( K_2 \) are the thermal conductivities of base fluid and particle, respectively, \( n \) and \( \nu \) are the particle shape factor and volume fraction, respectively; \( h \) is heat transfer coefficient, \( \delta_T \) is thickness of layer.

<table>
<thead>
<tr>
<th>Expression</th>
<th>Remarks</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>( K_{\text{eff}} / K_m = 1 + 3 \left[ \frac{(\alpha-1)\nu}{(\alpha+2)} - (\alpha-1)\nu \right] )</td>
<td>Maxwell Model</td>
<td>[12]</td>
</tr>
<tr>
<td>( K_{\text{eff}} / K_m = \left[ \alpha + (n-1) - (n-1)\alpha \right] / \left[ \alpha + (n-1) + (1 - \alpha)\nu \right] )</td>
<td>Hamilton-Crosser Model</td>
<td>13</td>
</tr>
<tr>
<td>( K_{\text{eff}} / K_m = 1 + 3\left[ \frac{(\alpha-1)\nu}{(\alpha+2)} - (\alpha-1)\nu \right] \left[ \nu + f(\alpha)\nu^2 + 0(\nu^3) \right] )</td>
<td>Davis model</td>
<td>[14]</td>
</tr>
<tr>
<td>( K_{\text{eff}} = K_m + (1-\nu) + K_2\nu + \nu h \delta_T )</td>
<td>Jang &amp; Choi model</td>
<td>[10]</td>
</tr>
<tr>
<td>( K_{\text{eff}} / K_m = \left{ 1 + A R_e^{0.333} \Phi \left[ 2(1-\nu) / (2+\nu) \right] \right} )</td>
<td>Prasher et al model</td>
<td>[11]</td>
</tr>
</tbody>
</table>

Key factors in understanding thermal properties of nanofluids are the ballistic nature of heat transport in the nanoparticles combined with direct or fluid mediated clustering effect that provide paths for rapid heat transport. Theoretical work, in the absence of a reliable experimental framework, has resulted in a large number of hypothesis, than systematic experimental results, to prove apparently anomalous phenomenon. Despite number of research studies on nanofluids, basic research remains at the initial stage, with results still to be reconfirmed and re-established. The size distribution of nanoparticles and nanoparticle aggregates in the suspensions is rarely reported. This lack of data can be attributed to the difficulty in properly characterizing high-concentration suspensions of nanoparticles.

**Thermal properties of nanofluids**

The conventional approaches and designs have reached their limit and cooling threatens to be the limit to both further miniaturization and increased speeds. One of the conventional approaches is to circulate cooling fluids in microchannels incorporated in a device. Here, the limitation eventually arises from the ability of the fluid to conduct heat away from hot surfaces. Thermal conductivity reflects the ability of a medium to conduct heat. Typically, liquids are better conductors than gases and vapours. For example, while air has a conductivity of the order of 0.03 W/(m K), water has a conductivity of the order of 0.6 W/(m K).

However many solids are even better conductors than liquids. Thus, even common red brick has a conductivity of 60 W/(m K), while metals like silver and copper have a conductivity of 400 W/(m K). An exotic material like the carbon nanotube (CNT) has a conductivity of 3000 W/(m K). One obvious solution to the cooling problem is to boost the conductivity of a fluid by using a suspension of particles of a highly conducting solid in it. However, the size of the microchannels prevents the use of conventional ‘fine’ particles, which are typically micron-sized, since they can clog the channels.

The below graph yields the thermal conductivity of different materials.

Nanoparticles are the obvious substitute candidates and can make the solution feasible. Thus, studying the thermal properties of nanofluids has grabbed the attention of scientists and engineers. Three main experimental observations have been made during studies on thermal properties of nanofluids, and have been summarized by Eastman et al.

The salient features are as follows.

First and this is the most enigmatic feature, it was found that thermal conductivity of a fluid was enhanced by large factors when nanoparticles were added up to only a small volume fraction. Thus, Lee et al. found that addition of 4% of Al₂O₃ particles increased thermal conductivity by a factor of 8%, while according to Eastman et al., particles of CuO at the same volume fraction enhance the conductivity by about 12%. This is interesting since conductivity of CuO is less than that of Al₂O₃.

![Thermal conductivity graph](image-url)
Metal particles have been found to be much more effective. Patel et al.3 found that even at as low a volume fraction of about 0.0001, thiol-protected gold particles increased thermal conductivity by 10%.

Other researchers have found greater enhancement with metal particles than with the lesser conducting oxide particles, though quantitatively less than that reported by Patel et al.17. Thus, ferrofluids containing 0.5% of iron particles were found4 to increase conductivity by 18%. Secondly, Das et al.18 found that thermal conductivity of nanofluids increased with increasing temperature. Clearly, this property is very advantageous in cooling applications.

Lastly, You et al.19 found that nanofluids exhibited three-fold increase in critical heat flux (CHF) over that of the liquid in which the particles were suspended. This parameter plays an important role in heat transfer where boiling is involved. All these features indicate the potential of nanofluids in applications involving heat removal. Issues concerning stability of nanofluids, since they do aggregate with ageing, have to be addressed before they can be put to use. Ironically, nanofluids of oxide particles are more stable but less effective in enhancing thermal conductivity in comparison with nanofluids of metal particles and CNTs. Though we will confine ourselves here to a discussion of enhancement of thermal conductivity, it is worthwhile to mention that enhancement of CHF may prove to be of wider utility.

Viscosity

Viscosity, like thermal conductivity, influences the heat transfer behaviour of cooling fluids. Nanofluids are preferred as cooling fluids because of their improved heat removal capabilities. Since most of the cooling methods used involve forced circulation of the coolant, modification of properties of fluids which can result in an increased pumping power requirement could be critical. Hence, viscosity of the nanofluid, which influences the pumping power requirements in circulating loops, requires a close examination.

Investigations [16, 17, 20-27] reported in the literature have shown that the viscosity of base fluids increases with the addition of nanoparticles.

Praveen et al. [26] measured the viscosity of copper oxide nanoparticles dispersed in ethylene glycol and water. An LV DV-II+ Brookfield programmable viscometer was used for the viscosity measurement. The copper oxide nanoparticles with an average diameter of 29 nm and a particle density of 6.3 g/cc were dispersed in a 60:40 (by weight) ethylene glycol and water mixture, to prepare nanofluids with different volume concentrations (1, 2, 3, 4, 5, and 6.12%). The viscosity measurements were carried out in the temperature range of -35 to 50°C.

The variation of the shear stress with shear strain was found to be linear for a 6.12% concentration of the nanofluid at -35°C, which confirmed that the fluid has a Newtonian behavior. At all concentrations, the viscosity value was found to be decreasing with an increase in the temperature and a decrease in concentration of the nanoparticles. The suspension with 6.12% concentration gave an absolute viscosity of around 420 centi-Poise at -35°C.

Nguyen et al. [28, 20, 27] measured the temperature and particle size dependent viscosity of Al2O3-water and CuO-water nanofluids. The average particle sizes of the samples of Al2O3 nanoparticles were 36 and 47 nm, and that of CuO nanoparticles was 29 nm. The viscosity was measured using a Viscolab450 Viscometer (Cambridge Applied Systems, Massachusetts, USA). The apparatus measured viscosity of fluids based on the couette flow created by the rotary motion of a cylindrical piston inside a cylindrical chamber. The viscometer was having an accuracy and repeatability of ±1 and ±0.8%, respectively, in the range of 0 to 20 centi-Poise.

The dynamic viscosities of nanofluids were measured for fluid temperatures ranging from 22 to 75°C, and particle volume fractions varying from 1 to 9.4%. Both Al2O3-water and CuO-water nanofluids showed an increase in the viscosity with an increase in the particle concentration, the largest increase being for the CuO-water nanofluid. The alumina particles with 47 nm were found to enhance viscosity more than the 36 nm nanoparticles. At 12% volume fraction, the 47-nm particles were found to enhance the viscosity 5.25 times, against a 3% increase by the 36-nm particles. The increase in the viscosity with respect to the particle volume fraction has been interpreted as due to the influence on the internal shear stress in the fluid. The increase in temperature has shown to decrease the viscosities for all nanofluids, which can be attributed to the decrease in inter-particle and inter-molecular adhesive forces.

An interesting observation during viscosity measurements at higher temperatures was the hysteresis behaviour in nanofluids. It was observed that certain critical temperature exists, beyond which, on cooling down the nanofluid from a heated condition, it would not trace the same viscosity curve corresponding to the heating part of the cycle. This was interpreted as due to the thermal degradation of the surfactants at higher temperatures which would result in agglomeration of the particles. The properties of oxides and their nanofluids, especially thermal conductivity, viscosity, and density of nanofluids are shown in Table 3. Wei Yu et al.29 discussed the properties of nanofluids and presented the below table.

Table 3. Properties of oxides and their nanofluids.
Thermal conductivity has been measured mostly using hot-wire method, but a few measurements have been made using the standard parallel-plate method.

Putnam et al.39 used a technique that is based on measurement of the extent of bending of a laser beam due to a gradient in refractive index caused by the temperature gradient, to measure thermal conductivity of nanofluids of thiol-protected gold particles. They report that the enhancements are in accordance with the theory of Maxwell! They have thrown down the gauntlet at fellow experimentalists and theoreticians by stating that ‘investigations of the properties of nanofluids have reached the awkward situation of having a greater number of competing theoretical models than systematic experimental results’. Thus it is clear that nanofluids will offer a lot more excitement, and perhaps controversy in the times to come.

**References**


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*Thermal conductivities of the oxides are for the corresponding bulk materials*


29. Wei Yu, Huaqing Xie School of Urban Development and Environmental Engineering, Shanghai Second Polytechnic University, Shanghai, 201209, China, “A Review on Nanofluids: Preparation, Stability Mechanisms and Applications”