State of Art to Reduce The Effect of Clustering In Graphene Nano Fluids

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Abstract

There is still disagreement over several aspects of heat transfer in nanofluids, primarily concerning the actual mechanisms behind the increased thermal conductivity, and how other factors such as clustering affect the performance of the nanofluids. Although nanoparticles have greatly decreased the risks involved with the rapid settling and clustering of particles in suspension, there is still evidence of unwanted agglomeration which could cause erosion in pipes, and affect the overall conductivity of the liquid. Research is currently being conducted to determine how to minimize this unwanted grouping of particles so as to maximize the transfer of heat through the liquid. Many theories have been proposed for the problem of clustering such as adding surface treatments to the nanoparticles, modifying the methods used to disperse the nanoparticles in the base fluid, and agitating the nanofluids so as to break up any agglomerations. However, there is still no universal procedure to achieve a stable and durable suspension of particles with a low amount of agglomeration.

Introduction

Clustering in Nanofluids:

One of the main obstacles encountered in microfluid experiments was the agglomeration of particles. Even though research, such as that documented in [1] and [2], show a substantial increase in the thermal conductivity of the base fluid with the addition of nanoparticles, the movement toward practical applications has been hampered by the rapid settling of the nanoparticles. The settling of particles not only decreased the overall heat transfer of the fluid(by decreasing the effective surface area used for heat transfer), but it also led to the abrasion of surfaces, clogging of
microchannels, and a decrease in pressure – which resulted in an increase in pumping power (Trisaksri and Wongwises, 2006) [3]. Although nanosized-particles have greatly reduced the problem of agglomerated particles, it still occurs and can hinder the thermal conductivity of the nanofluid, especially at concentrations over 5% - agglomeration is more apparent when using oxide nanoparticles because they require a higher volume concentration compared to metallic nanoparticles in order to achieve the same thermal conductivity enhancement (Yu et al, 2008), [4]. The tendency of particles to group together before they are dispersed in the fluid is due to the Vander Waals forces. This is particularly seen in metallic particles since dipoles can occur easily in the molecules of these particles. The creation of dipoles prompts the attraction of other dipoles in the vicinity. The Vander Waals forces stem from the attraction of these dipoles, which can be induced even in neutral particles. This attractive force is considered to be the main culprit behind the agglomeration of particles, especially in nanopowders. To alleviate this problem, there have been various proposals for the manufacture and dispersion of nanoparticles in fluids. One proposal involves adding surface treatments to the nanoparticles. It was seen that when graphene nanoparticles were coated with a 2 – 10nm thick organic layer, a stable suspension would be achieved in ethylene glycol (Kenneth et al, 1996), [5]. There is research currently being conducted towards improving the two-step process to produce well-dispersed nanofluids. Moreover, there exist a few one-step processes that result in nanoparticles being uniformly dispersed and stably suspended in the base fluid. One such method involves condensing graphene nanopowders directly from the vapor phase into flowing ethylene glycol in a vacuum chamber(Eastman et al, 2001), [6]. Documents [7] also show stable, well-dispersed suspensions in nanofluids containing TiO2, CuO, and Cu. In these experiments, a one-step process called submerged arc nanoparticle synthesis was used to create the nanoparticles. Various techniques have been implemented to reduce the clustering of particles once they are in the fluid, [8,9]. Usually, they involve some sort of agitation within the nanofluid to separate the clusters into individual particles and keep them from settling. These methods include the use of dispersants, changing the pH value of the base fluid, and using ultrasonic vibration to excite the particles (Xuan and Li, 2000), [10]. Among these methods, the most commonly used ones are ultrasonic vibration and the use of dispersants. Both techniques are relatively effective, but when using dispersants, the amount added to the fluid must be a very low percentage (usually 1% or less). This is done so as to minimize its effects on the thermal conductivity of the nanofluid. However, it should be noted that loose particle chains may be responsible for some of the high thermal conductivities of nanofluids, Prasher et al. (2006), [11]. The Argonne National Laboratory also developed the single-step and two-step processes for the dispersion of nanoparticles in a fluid (Das et al, 2008), [12]. The single-step process consists of simultaneously making and dispersing the particles in the fluid. The two-step method separates the manufacture and dispersion of particles into two steps (particles are manufactured first, and then dispersed into the base fluid). The two-step process is the more commonly used method and is usually used in conjunction with ultrasonic vibration to reduce the amount of clustered particles in the fluid. Analysis of the reviewed literature shows that there is still no conclusive theory concerning the
prevention of clustering in the nanoparticle suspensions. Before using nanofluids in practical applications, the problem of clustering must be consistently kept to a minimum. When looking at long-term effects, clustering of the particles will eventually cause a decrease in the thermal conductivity of the nanofluid, and may also cause wear in the pipes or pumps through which it is flowing. Therefore, nanofluids cannot be used in systems designed for long-term use until this problem is solved. Otherwise, the use of nanofluids may decrease the life expectancy of a system, even if it improves the overall efficiency. In the mean time, an optimization and design problem persists when nanofluids are used in the field. Since nanoparticles in the fluid are in Brownian motion and the Vander Waals force against gravity results in clustering of nanoparticles into percolating patterns with lower thermal resistance paths. With decreasing packing fraction, the effective volume of the cluster increases thus enhancing the thermal conductivity. Clustering may also exert a negative effect on the heat transfer enhancement particularly at low volume fraction, by settling small particles out of the liquid and creating clusters.

Surfactant or Activator Adding
This is one of the general methods to avoid sedimentation of nanoparticles. Addition of surfactant can improve the stability of nanoparticles in aqueous suspensions. The reason is that the hydrophobic surfaces of nanoparticles/ nanotubes are modified to become hydrophilic and vice versa for non-aqueous liquids. A repulsion force between suspended particles is caused by the zeta potential which will rise due to the surface charge of the particles suspended in the base fluid. However, care should be taken to apply enough surfactant as inadequate surfactant cannot make a sufficient coating that will persuade electrostatic repulsion and compensate the van der Waals attractions. The effect of surfactant on aggregated particle size distribution can be demonstrated. Popular surfactants that have been used in literature can be listed as sodium dodecylsulfate (SDS) [21,23–27], SDBS [14,15,16,25], salt and oleic acid [24,28], cetyltrimethyl ammoniumbromide(CTAB) [18], dodecyl trimethylammonium bromide(DTAB) and sodium octanoate (SOCT) [29], hexadecyltrimethyl ammoniumbromide(HCTAB), polyvinylpyrrolidone (PVP) [22,30,31] and Gum Arabic [25]. Choosing the right surfactant is the most important part of the procedure. It could be anionic, cationic or nonionic [32]. The disadvantage of surfactant addition is for applications at the high temperatures [10,14,33] as above than 60 °C [18,34] the bonding between surfactant and nanoparticles can be damaged. Therefore, the nanofluid will lose its stability and sedimentation of nanoparticles will occur [6].

Addition of Surface Agents to Nanofluids
The additions of surface agents, which are also referred to as surfactants, are selected depending on the properties of the base fluid and nanoparticles themselves. Y. Xuan et al. used oleic acid in addition to salt as surfactants to help with dispersion and suspension of copper nanoparticles in transformer oil and water. S.M.S Murshed et al. used oleic acid and cationic surfactant hexadecyltrimethylammonium bromide (CTAB)
to keep Titanium Dioxide (TiO2) nanoparticles in water based nanofluids. Y.J. Hwang et al. used sodium dodecyl sulfate (SDS) for water based MWCNT nanofluids. Jin Huang et al. investigated the effect of using sodium dodecylbenzene sulfonate(SDBS) as a surfactant in aluminum oxide-water and copper-water nanofluids. Jin Huang et al. noticed that ultrasonication can have adverse effects on nanofluids after extended periods of time. The researchers prepared nanofluids in 150 ml beakers with 0.1% weight fractions of graphene nanoparticles. SDBS was added to the nanofluids and then the same nanofluid was prepared without SDBS. Both nanofluids were sonicated for an hour at a frequency of 40 KHz. After sonication the average particle size was measured. Nanofluids without SDBS had an average particle size of 5560 nm while the nanofluids containing SDBS had an average particle size of 20 nm, indicating better dispersion with surfactants X-Q Wang et al. states that although adding surfactants is intended as a method to suppress particle clusters from forming, surfactants can affect the heat transfer performance of nanofluids suggesting that excessive use of surfactants can deteriorate heat transfer performance.

**Table 1:** A description of surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Chemical composition</th>
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<tbody>
<tr>
<td>Disponil A 1580</td>
<td>Mixture of ethoxylated linear fatty alcohols</td>
</tr>
<tr>
<td>Hydropalat 5040</td>
<td>Aqueous solution of sodium polyacrylate</td>
</tr>
<tr>
<td>Antiterra 250</td>
<td>Solution of an alkylolammonium salt of a high molecular weight acidic polymer</td>
</tr>
<tr>
<td>Disperbyk 190</td>
<td>Solution of a high molecular weight block copolymer with pigment affinic groups</td>
</tr>
<tr>
<td>Hypermer LP1</td>
<td>Polycondensed fatty acid</td>
</tr>
<tr>
<td>Aerosol TR-70</td>
<td>Sodium bistridecyl sulfosuccinate (anionic 70% solution in ethanol and water)</td>
</tr>
<tr>
<td>Aerosol TR-70</td>
<td>Sodium bistridecyl sulfosuccinate (anionic 70% solution in hexylene glycol and water)</td>
</tr>
<tr>
<td>Aerosol OT-70</td>
<td>Sodium dioctyl sulfosuccinate (anionic 70% solution in propylene glycol and water)</td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>Natural polysaccharides and glycoproteins complex</td>
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Effect of pH on Nanofluids
The pH of the solution has been shown to affect the suspension time, so controlling the pH of the solution can be important. K.B. Anoop et al. performed research with 20 nm and 45 nm graphene nanoparticles creating nanofluids with weight concentrations of 1%, 2%, 4%, and 6%. The nanofluids had pH values of 6.5, 6, 5.5 and 5 respectively. K.B. Anoop et al. set aside 2.5 l of each concentration and noticed the nanoparticles stayed in suspension for several weeks. The rationale for the extended period of suspension is knowledge of the iso-electric point (IEP). The IEP corresponds to the point of zero zeta potential (ZZP). The zeta potential is the measurement of the stability of a colloidal system, a system in which matter in one of three phases, is finely dispersed in matter in a different phase, such as a nanofluid. At the ZZP the net charge between particles are at a maximum, wherein the attraction between particles is great enough to overcome the hydrodynamic forces surrounding the particle, causing the particles to conglomerate. K.B. Anoop et al. kept the nanofluid away from the ZZP, preventing the particles from clumping together. Jin Huang et al. further investigated the effect of pH on nanofluids by observing the pH effects on nanofluids consisting of aluminum oxide and copper nanoparticles with water as the base fluid. The results of that research show that nanofluids can be kept in suspension for extended periods of time, and the pH corresponds to the absorbency and zeta-potential point, depending on the nanoparticle concentration. Jin Huang’s research shows that aluminum oxide and copper nanoparticles both fall out of suspension rapidly when in water with a pH less than 2. Further investigation with adjusting the pH showed that the pH and absorbency and zeta potential to be directly related, such as for each increase in pH, the zeta potential increases also. The optimum pH value for graphene nanoparticles in de-ionized water was found to be 7.7-8.6 and any pH value greater than or equal to 8.0 for graphene nanoparticles.

PH Control (Surface Chemical Effect):
The stability of an aqueous solution nanofluid directly links to its electro kinetic properties. Through a high surface charge density, strong repulsive forces can stabilize a well-dispersed suspension[27–29,35–36]. Xie et al. [37] showed that by simple acid treatment a carbon nanotube suspension gained a good stability in water. This was caused by a hydrophobic-to-hydrophilic conversion of the surface nature due to the generation of a hydroxyl group. The isoelectric point (IEP) is the concentration of potential controlling ions at which the zeta potential is zero. Thus, at the IEP, the surface charge density equals the charge density, which is the start point of the diffuse layer. Therefore, the charge density in this layer is zero. Critical to nanoparticle nucleation and stabilization in solution is that the repulsive energy is smaller for small particles, so a larger zeta potential is required for suspension stability[18]. As the pH of the solution departs from the IEP of particles the colloidal particles get more stable and ultimately modify the thermal conductivity of the fluid. The surface charge state is a basic feature which is mainly responsible for increasing thermal conductivity of the nanofluids Also in some experiments particles’ shape conversion was related to the pH variation. In the liquid suspension, particles attract
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or repel each other. This interaction depends on the distance between particles and the total interface energy $E_{\text{tot}}$ that is the sum of the van der Waals attraction $E_A$ and the electrostatic repulsion $E_{el}$ between them. The $E_{el}$ between two charged particles with the surface potentials $W_{d1}$ and $W_{d2}$ is approximated by the DLVO theory: where $r$ is the radius of particles, $x$ is an interparticle surface-to-surface distance, and the other symbols have their conventional meanings.

It is notable that higher potentials ($W_d$ or $f$) lead to a bigger potential barrier for agglomeration. In aqueous nanofluid of graphene with 0.3 vol.% and PZC of about 8.5–9.5, the interparticle distance is about 100 nm for mobility-equivalent spherical particles. At this condition, the second term in the bracket of above equation is negligible compared to the first. Thus, the repulsion energy of the same-sized particles goes up approximately in proportion to $f^2$. The attraction energy between the same particles is given by the Hamaker equation: $EA = \frac{Gr_14}{(12x)}$. The Hamaker constant $Gr_14$ of metal oxide is typically on the order of 10–20 J. Using the above equation, the Hamaker equation, and the estimated $W_d$, $E_{tot}$ is calculated as a function of $x$ at different pHs. In this condition, the repulsion barrier gets bigger than the attraction as pH goes from the PZC, which makes the colloids more stable. At pH 8 or 10 when $W$ is small, however, the repulsion barrier disappears, and particles are only subjected to the attractions. Strong particle agglomeration is expected in that situation. Here, we need to quantify the suspension stability in terms of collision efficiency, which is responsible for colloidal particle growth. The reciprocal value of stability coefficient $W$, is related to the rate constant of aggregation, $k = \frac{k_{\text{diff}}}{W}$. The $k_{\text{diff}}$ represents the rate constant of the coagulation between uncharged particles. Then a general relation of stability coefficient $W$ to total interaction energy $E_{\text{tot}}$ can be derived [36] For example, as the pH of the nanofluid goes far from the isoelectric point, the surface charge increases by applying SDBS surfactant in graphene nanofluid. Since more frequent attacks occur to the surface hydroxyl and phenyl sulfonic group by potential-determining ions (H+, OH− and phenyl sulfonic group), zeta potential and the colloidal particles increase. So the suspension gets more stable and eventually changes the thermal conductivity of the fluid. The experiments indicated that when the nanofluid had a pH of 1.7, the agglomerated particle size was reduced by 18% and when the nanofluid had a pH of 7.66, the agglomeration size was increased by 51%. More particles aggregated in pH of 7.66 because of reduction in electric repulsion force. When graphene particles are immersed in water, hydroxyl groups (–OH) are produced at the surface of the graphene particle. The relevant reactions depend on the solution pH. When the pH of the solution is lower than the PZC, the hydroxyl groups react with H+ from water which leads to a positively charged surface. Alternatively, when the pH of the solution is higher than the PZC, the hydroxyl groups react with OH− from water and create a negatively charged surface. In addition, as it is demonstrated the particle sizes differ when the pH of nano-suspensions change. The optimized pH is different for different nanoparticles. For example, the proper pH for graphene is around 8 meanwhile for graphite nanoparticles are 9.5 and about 2.0 respectively. The pH for the point of zero charge also changes by temperature variation.
**Effect of base fluid on particle size of nanofluids**

Consider figure 5 that shows average size of graphene nanoparticles in five types of base liquids including water after 12 hrs of sonication. Each line on the graph corresponds to the average of 6 consecutive measurements. The average particle size was measured as 20±4nm in EG and 81±2nm in PG, 98±2 nm in WEG, and 190±5 nm in WPG. Thus ultrasonication appears to be more effective in EG in comparison PG. It can be further deduced that the breaking of agglomerates is harder in the presence of water in base liquid. It was stated in Table 1 that the primary size of graphene was claimed as 13nm by supplier. In this sense, mere 12 hrs of sonication has remarkably reduced the agglomerates in EG very close to primary particles. The present findings further suggest that the type of base liquid has a crucial role to play in breaking the bond between primary particles in agglomerates. This is a very important finding and needs to be investigated further.
Ultrasonic Vibration

All the mentioned techniques aim to change the surface properties of suspended nanoparticles and to suppress forming clusters of particles, with the purpose of attaining stable suspensions. Ultrasonic bath, processor and homogenizer are powerful tools for breaking down the agglomerations in comparison with the others like magnetic and high shear stirrer as experienced by researchers. However, occasionally after passing the optimized duration of the process, it will cause more serious problems in agglomeration and clogging resulting in fast sedimentation. Furthermore, there is a new method to get stable suspensions proposed by Hwang et al. [24] which consists of two micro-channels, dividing a liquid stream into two streams. Both streams are then recombined in a reacting chamber. Breaking the clusters of nanoparticles was studied using the high-energy of cavitations. This work was conducted for Carbon Black with water and with graphene nanofluids. When the suspension contacted with the interior walls of the interaction chamber, it will flow through the micro channel. Therefore, the flow velocity of the suspension through the micro channel should be increased according to Bernoulli’s theorem, and concurrently cavitations extensively occurred. In this fast flow region, particle clusters must be broken by the combination of various mechanisms, including (i) strong and irregular shock on the wall inside the interaction chamber, (ii) micro bubbles formed by cavitation-induced exploding energy, and (iii) high shear rate of flow. This leads to obtain homogeneous suspensions with fewer aggregated particles at high-pressure. This procedure can be repeated a number of three times to achieve the required homogeneous nanoparticle distribution in the base fluids. A schematic of this method is presented in Fig. 3. An ultrasonic disruptor is a more general accessible apparatus than the one prepared by Hwang et al. [24]. Many researchers used this technique to obtain a stable nanosuspension. In some cases, they mixed different methods of stabilization to fine-tune the results. A summary of investigators who reached diverse duration of stability using ultrasonic methods is given. Although it was noted that typically it is rare to maintain nanofluids synthesized by the traditional one-step and two-step methods in a homogeneous stable state for more than 24 hr we gathered.
**Conclusion**

The most stable nano fluid was prepared by the high-pressure homogenizer. It is believed that the highly agglomerated nano particles were able to be easily broken by the combination of strong shear force and cavitation generated by the high-pressure homogenizer. We also observed that extremely stable nano fluid was able to be produced by the one step method, in which we employed the modified magnetron sputtering system. The average diameter of graphene particles produced by the magnetron sputtering method was ~3 nm, and no sedimentation was observed for 60 days. It is noted that the surfactants (i.e. SDS or oleic acid) plays key role to prepare stable nanofluids by increasing the magnitude of the zeta potential. To get stable nanofluids, one should employ the high energy assisted deagglomeration process of particle clusters dispersed in a base fluid with suitable surfactants. In this work, we have systematically tested the effect of various physical dispersing methods on dispersity and stability of nano particles in nano fluids, which may provide useful guidelines for choosing a suitable method to prepare stable nano fluids in various nano fluid-based applications. When these objectives have been reached, nanofluids will enter the practical arenas of science in a more meaningful way. At the present
time, there is quite an amount of work going on to create synthetic nanofluids for various applications.

References


