Heat Transfer Mechanisms in Nanofluids: A Review

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Abstract: Traditional heat transfer fluids, such as water, ethylene glycol and lubricating oil which are used in various applications such as chemical processes, refrigeration, heating and cooling processes, transportation, power generation and other micro-sized applications have poor heat transfer properties and impose limitation to heat transfer augmentation. Improving the thermal conductivity is the key idea to improve the heat transfer characteristics of conventional fluids. Since a solid matrix has a larger thermal conductivity relative to base fluid, suspending solid fine particles (millimeter or micrometer sized range) into the base fluid is expected to improve the thermal conductivity. A dilute suspension of nanometer-sized particles dispersed in a base fluid is known as Nanofluids. Nanofluids exhibit enhanced heat transfer properties and are expected to be a promising coolant candidate for thermal management systems of next generation.

Keywords: Nanofluids, Heat transfer enhancement, Thermophysical properties

1. Introduction

Over a century ago, researchers have tried to increase the thermal conductivity of suspensions by adding solid fine particles but those techniques are discarded due to associated drawbacks with them. However, the recent advances in nanotechnology have made it possible to produce particles with nano-sized order (nanoparticles) with relative ease. Innovative idea of suspending these nanoparticles in a base fluid for improving thermal conductivity has been proposed recently [1-3]. These new class of fluids are called ‘nanofluids’. Nanofluids were introduced in 1995 [4] by Choi in Argonne National Laboratory (ANL). Due to their small size, nanoparticles can easily fluidize inside the base fluid, and as a result, the clogging of channels and erosion in channel walls are no longer a problem. Compared with suspended particles of millimeter or micrometer dimensions, nanofluids show not only better suspension stability and rheological properties, but also higher thermal conductivity. Earlier studies have shown that there is about 40% enhancement in thermal conductivity of nano-fluids is possible with 0.3 vol. % of copper nanoparticles of about 10 nanometer size [5]. This shows thermal conductivity enhancement at nano-scales not only volume but also size dependent. The ratio of surface area to volume is 1000 times greater for particles with a 10 nm diameter than that for particles with 10 μm diameter. The much larger surface area of nanoparticles relative to those of conventional particles should not only improve heat transfer capabilities, but also increase the stability of suspensions. Nanofluids offer a unique combination of the two features most highly desired for thermal engineering applications: good stability against sedimentations and ultra-high thermal conductivity. By suspending nanoparticles inside the base fluid, the heat transport performance of the fluid can be significantly improved [2]. The main reasons may be listed as follows:

1) The suspended nanoparticles increase the surface area and the heat capacity of the fluid.
2) The suspended nanoparticles increase the effective (or apparent) thermal conductivity of the fluid.
3) The interaction and collision among particles, the surface of fluid and the flow passage are intensified.
4) The dispersion of nanoparticles flattens the transverse temperature gradient of the fluid.

2. Nanofluid Synthesis Techniques

Many different particle materials are used for nanofluid preparation, Al₂O₃, CuO, TiO₂, SiC, TiC, Ag, Au, Cu, and Fe nanoparticles are frequently used in research. However, these particles show different thermal conductivity enhancement and are not related anyway. Spherical particles are mostly used in nanofluids for the simplicity of analysis.

One Step Method

Preparation of nanofluids is the first key step in the application of nanofluid cooling technology. In the one-step technique, the production of nanoparticles and dispersion of nanoparticles in the base fluid are combined into a single step. There are some variations of this technique. In one of the common methods, named direct evaporation one step method, the nanofluid is produced by the solidification of the nanoparticles, which are initially gas phase, inside the base fluid [5]. The dispersion characteristics of nanofluids produced with one-step method are better than those produced with the two-step technique [6]. The main drawback of this technique is that they are not proper for mass production, which limits their commercialization [6].

Two Step Method

In the two-step technique, the first step is the production of nanoparticles and the second step is the dispersion of the nanoparticles in a base fluid. Two-step technique is advantageous when mass production of nanofluids is considered, because at present, nanoparticles can be produced in large quantities by utilizing the technique of inert gas condensation [7]. The main disadvantage of the two-step technique is that the nanoparticles cluster during the preparation of the nanofluid which prevents the proper dispersion of nanoparticles inside the base fluid. [6].

3. Enhancement Mechanisms and Associated Models

Different authors proposed different mechanisms of heat transfer in nanofluids [19-22]. The proposed mechanisms for
the anomalous enhancement discussed in the open literature are:

Brownian Motion of Nanoparticles

Unlike larger sized particles, nanoparticles are not static in solution. As particle dimensions get smaller and smaller (particularly of nano-sized order), it becomes increasingly difficult to hold them in place. They have a natural tendency to move around and hence Brownian diffusion or motion becomes a major effect. Brownian motion is the random motion of particles suspended in a fluid at very high rates. This random motion transports energy directly by nanoparticles. The energy exchange in the direct nanoparticle-nanoparticle contact arising from the particle collisions in the nanofluid could result in an enhancement of the thermal conductivity. Brownian motion is a very small fraction of the thermal conductivity of the base fluid. This fact was verified by molecular dynamics simulation [33]. As a result, it was concluded that Brownian motion of nanoparticles could not be the main cause of anomalous thermal conductivity enhancement with nanofluids. Many models were developed for the determination of thermal conductivity of nanofluids based on the Brownian motion of nanoparticles. Jang and Choi [24] modelled the thermal conductivity of nanofluids by considering the effect of random motion i.e. Brownian motion of nanoparticles. The proposed model is a function of not only thermal conductivity of the base fluid and nanoparticles but it also depends on the temperature and size of nanoparticles. Energy transport in nanofluids was considered of four modes; heat conduction in the base fluid, heat conduction in nanoparticles, collision between nanoparticles (due to Brownian motion) and micro-convection caused by the random motion of the nanoparticles. Among these, the collisions between nanoparticles were found to be negligible when compared to other modes. As a result of the consideration, the following expression was presented:

\[ k_{\text{eff}} = k_f (1 - \phi) + k_p^* \phi + 3C_1 \frac{d_f}{dp} k_f \text{Re} d^2 \text{Pr} \phi \]  
(1)

Where \( C_1 \) is proportionality constant, \( d_f \) is the diameter of fluid molecules, \( \text{Pr}_f \) is the prandtl number of base fluid and \( k_p^* \) is defined so that it also includes the effect of Kapitza resistance. Koo and Kleinsteufer [12] considered the effect of Kapitza resistance. They proposed an equation to predict the thermal conductivity of suspensions of solid particles in nanofluids:

\[ k_{\text{eff}} = k_f + 2k_m - 2\phi(k_m - k_p) + \rho_p C_{p,m} \frac{k_BT}{2k_m 3\pi r^2 d^3} \]  
(3)

\( r_{cl} \) is the apparent radius of the nanoparticle clusters, which should be determined by experiment. The first term on the right hand side of equation (3) is the Maxwell model for thermal conductivity of suspensions of solid particles in fluids. The second term on the right side of above equation adds the effect of random motion of nanoparticles into account. For the contribution of this term, the following values were presented for Cu (50nm)/ water nanofluid: For \( \phi = 0.03 \% \), contribution of the second term is 11% when clustering occurs and 17% when clustering does not occur. For \( \phi = 0.04 \%\), contribution of the second term is 14% when clustering occurs and 24% when clustering does not occur. It was indicated that Brownian motion of nanoparticles become more effective with increasing volume fraction. On the other hand, as nanoparticles (or clusters) become larger, their random motion becomes slower and this decreases the enhancement in thermal conductivity. It is concluded that severe clustering had adverse effect on thermal conductivity.

Interfacial Layer Effect around Nanoparticles

Liquid molecules are known to form ordered layered structures (shells or solid like liquid layer) at solid surfaces and these interfacial layers have different thermophysical properties from the bulk liquid and solid particles. Because of the ordered structure of the nanolayer, it is expected to have higher thermal conductivity than the bulk liquid [22]. The thickness of this solid like layer of liquid molecules at the interface of particles play an important role in heat transportation from solid to adjacent liquid. For particles of micro-meter size, the surface areas are small, e.g., for
alumina powders with an average diameter of 10 µm, their SSA (Specific Surface Area) is only 0.15 m²·g⁻¹. Therefore the effect of interfacial layer is negligible. However, nanoparticles have large SSA, e.g., for alumina powders, with an average diameter of 10 nm, their SSA is as large as 151 m²·g⁻¹ which is much larger compared to micro-sized particle. Thus, the interfacial layer effect around nanoparticle plays a significant role in heat transfer between nanoparticles and base fluid. Various authors have proposed the mathematical models for finding effective thermal conductivity of nanofluid considering interfacial layer formed on particles. Yu & Choi [25] developed a model for the thermal conductivity of non aggregated particles in nanofluid considering the effect interfacial layer around the nanoparticles, and is expressed as:

\[
k_{\text{eff}} = \frac{k_{pe} + 2k_m + 2(k_{pe} - k_m)(1 + \delta)^3 \phi}{k_{pe} + 2k_m - (k_{pe} - k_m)(1 + \delta)^3 \phi} k_m
\]  

(4)

Based on effective medium theory, the equivalent thermal conductivity \((k_{pe})\) of the equivalent particles can be calculated as [25]:

\[
k_{pe} = \frac{[2(r_p)^3(k_p - k_i) + (r_p + t)^3(k_p + 2k_i)]k_i}{k_i - k_p + (r_p + t)^3(k_p + 2k_i)}
\]

And,

\[
\delta = \frac{t}{r_p}
\]

Xie et al. [29] proposed a model for the effective thermal conductivity of nanofluid considering the effect of interfacial nanolayer and expressed as:

\[
k_{\text{eff}} = k_m + 3\theta \phi k_m + \frac{3\theta^2 \phi^2}{1 - \theta \phi} k_m^2
\]

(5)

Where,

\[
\theta = \frac{\left(\frac{k_i - k_m}{k_i + 2k_m}\right)(1 + \delta)^3 - \left(\frac{k_p - k_i}{k_p + 2k_i}\right)}{(1 + \delta)^3 + 2\left(\frac{k_i - k_m}{k_i + 2k_m}\right)\left(\frac{k_p - k_i}{k_p + 2k_i}\right)}.
\]

\[
\phi = \phi(1 + \delta)^3
\]

and,

\[
k_e = \left[\frac{k_e}{k_e(1 + \delta) - 1} - \delta \ln \left(1 + \frac{k_e}{k_e(1 + \delta) - 1} \right) + \delta \frac{k_e}{k_e(1 + \delta) - 1}\right]
\]

(6)

Mintsa et. al. [30] derived an empirical relation on the basis of experimental data as:

\[
k_{\text{eff}} = [1.72\phi + 1.0]k_m
\]

(7)

Feng et al. [31] proposed a one-dimensional heat conduction model comprising equivalent particle \((r_p + t)\) and used the thermal-electrical analogy technique to evaluate the effective thermal conductivity for the cluster as:

\[
k_{\text{agg}} = \left[\left(1 - \frac{3}{2}\phi_e\right)k_m + \frac{3k_m\phi_e}{\beta} \left[\frac{1}{\beta} \ln \frac{1}{1 - \beta} - 1\right]\right]
\]

(8)

Where, \(\beta = 1 - \frac{k_m}{k_{pe}}\)

The effective thermal conductivity of nanofluid is a function of thermal conductivity of interfacial nanolayer. It is also fact that some nanoparticles in nanofluid are in contact with each other forming clusters. Feng et al. [31] proposed a model for combined effect of volumetric proportion of aggregate and non aggregate particles as:

\[
k_{\text{eff}} = \phi k_{\text{agg}} + (1 - \phi) k_{\text{non-agg}}
\]

(9)

The above equation (9) shows that the effective thermal conductivity depends upon the effective volume fraction, thermal conductivity of aggregate and non-aggregate particles. In the above equation the values of effective conductivities of non aggregate and aggregate nanofluid, has been taken from equations (4) and (8) respectively.

Ballistic Phonon Transport in Nanoparticles

Macroscopic theories assume that the heat is transported by diffusion. In crystalline solids, heat is carried by phonons, that is, by the propagation of lattice vibration. Such phonons are created at random, propagate in random directions and are scattered by each other or by defects. When the size of the nanoparticles in a nanofluid becomes less than the phonon mean- free path, phonons are no longer diffuse across the nanoparticle but move ballistically without any scattering [23]. Therefore, the ballistic phonons initiated in one particle can persist in the liquid and reach a nearby particle even though the phonon mean free path in liquid is very short (~1-2nm). This process can further largely by agitated by the random motion of nanoparticles. Therefore, this particular thermal transport process can increase the thermal conductivity to a larger extent.

Thermophysical Properties

Over the years, a significant amount of experimental and theoretical research was made to investigate the thermophysical behaviour of nanofluids. In the studies, it was observed that a high thermal conductivity enhancement could be obtained with nanofluids. Many researchers proposed theoretical models to explain and predict that anomalous behaviour of thermal conductivity.

Thermal Conductivity

There are no theoretical formulas currently available to predict the effective thermal conductivity of nanofluids satisfactorily. A variety of theoretical models have been developed to predict the effective thermal conductivity of nanofluids. Maxwell [10] proposed a model for effective thermal conductivity \((k_{\text{eff}})\) of suspension of solid particles \((k_p)\) in the based fluid of conductivity \((k_m)\) for low volume fraction \((\phi)\) of spherical particles and is given by:

\[
k_{\text{eff}} = \frac{k_p + 2k_m + 2\phi(k_p - k_m)}{k_p + 2k_m - \phi(k_p - k_m)} k_m
\]

(10)
Hamilton Closser [15] proposed a model with considering the effect of shape of the solid particles in base fluid resulting in:
\[ k_{\text{eff}} = \frac{k_p + (n-1)k_m - (n-1)p\phi(k_m - k_p)}{k_p + (n-1)k_m + \phi(k_m - k_p)} \] (11)

Where, empirical shape factor and is defined as \( n = \frac{3}{\psi} \), where \( \psi \) = sphericity

Jeffrey [5] modified the Maxwell’s equation by taking into account the effects of particle-particle interaction:
\[ k_{\text{eff}} = 1 + 3\alpha + \left( 3\beta^3 + \frac{3\beta^3}{4} + \frac{9\beta^5}{16} + \frac{3\beta^5}{64} + \ldots \right) \phi^2 \] (12)

Where \( \alpha \) is the thermal conductivity ratio, \( \frac{K_{\text{eff}}}{K_m} \) and \( \beta \) is defined as
\[ \beta = \frac{\alpha - 1}{\alpha + 2} \] Equation (12) is accurate up to order of \( \phi^2 \). The higher-order terms represent pair interactions of randomly dispersed spheres.

Viscosity
Drew and Passman [14] suggested the well-known Einstein’s equation [20] for calculating viscosity, which is applicable to spherical particle in volume fraction less than 5.0 vol. % and is defined as follows:
\[ \mu_{nf} = \mu_{bf} \left( 1 + 2.5\phi \right) \] (13)
Batchelor [16] modified this equation for spherical particles as follows:
\[ \mu_{nf} = \mu_{bf} \left( 1 + 2.5\phi + 6.2\phi^2 \right) \] (14)

Brinkman [17] extended the Einstein’s equation for volume fraction less than 4% as:
\[ \mu_{nf} = \mu_{bf} \left( 1 - \phi \right)^{1.35} \] (15)

Where \( \mu_{bf} \) is the viscosity of the nanofluid and \( \mu_{bf} \) is the viscosity of the base fluid.

Density and Heat Capacity
The correlation suggested by Pak and Choi [8] is found to be an appropriate way to estimate the density as well as heat capacity necessary to simulate the flow characteristics of a nanofluid. These thermophysical properties are expressed as weighted average of base fluid and nanoparticle properties. In most computational studies, these relations are used which are indicated in terms of particle volume fraction:
\[ \rho_{nf} = (1-\phi)\rho_{bf} + \phi\rho_p \] (16)
\[ C_p = (1-\phi)C_{p,bf} + \phi C_{p,p} \] (17)

4. Applications
The novel and advanced concepts of nanofluids offer fascinating applications over a wide range from automotive cooling to biomedical field. Their practical applications are yet to be explored to the fullest once the science and engineering of nanofluids are fully understood. Some of the research work under the application of nanofluid is enlisted below:

Leong et al. [32] studied the application of ethylene glycol based copper nanofluids in an automotive cooling system. They observed that overall heat transfer coefficient & heat transfer rate in engine cooling system increased with the usage of nanofluids compared to ethylene glycol alone. They showed that about 3.8% of heat transfer enhancement could be achieved with the addition of 2% copper particle in a base fluid at Reynolds number 6000 and 5000 for air & coolant respectively. Nanofluids can also be effectively used for a wide variety of industries, ranging from transportation to energy production and in electronics systems like microprocessors, Micro-Electro-Mechanical Systems (MEMS) and in the field of biotechnology. A nanofluid coolant could flow through tiny passages in MEMS to improve its efficiency [35].

Applications of nanofluid in medicine and biology are also fast growing. One such application is laser surgery. Pulsed lasers are used extensively in laser surgery as nanoblades. A tightly focused laser beam is well capable of inducing hot localized plasma for rapid heating to destroy the tumor cells. Hot local spots will indiscriminately ruins healthy and cancerous cells. Efficient and fast heat dissipation is critical to save the healthy cells in close proximity to targeted tumor cells. Creating a nanofluid environment surrounding the tumor cells will effectively act as a heat sink to preserve the health tissues [34].

Nanofluids are promising and efficient fluids from thermal performance viewpoint. Research about nanofluid is fast growing and the challenges in the production of nanofluids are to develop new methods to cost-effective mass production of nanofluids at an industrial-scale for commercial applications. In ideal case, a method that does not need vacuum system and show capabilities to provide continuous fluid feed and nanofluid extraction is the potential candidate.

5. Concluding Remarks and Future Scope
The present review provides a comprehensive outline of various potential heat transfer enhancement mechanisms in nanofluids. Considerable research progress in the field of nanofluids has been pointed out. This review aims to provide an overview of various research work undertaken in the regime of heat transfer enhancement in nanofluids.

At present, there is significant discrepancy in thermal conductivity data of nanofluids. For practical application of nanofluids as ‘cooling fluids’, these discrepancies should be minimised or eliminated if possible by systematically investigating the effects of various parameters on the thermal conductivity. These parameters could include the effect of agglomeration, pH value of the suspension, non-dispersion of these nanoparticles in the base fluids etc. The characterization of these nanoparticles should be properly understood to make use of nanofluids in real scenario.
In the literature, there are many models to predict the effective thermal conductivity of nanofluids but there is no single model which determines the effective thermal conductivity of nanofluids taking all possible mechanisms of heat transfer enhancement into account. The concept of keeping ‘well dispersed’ nanoparticles in the suspension by using acoustic field can be thought of as a future work in this regard. Also some work in ‘nano-particle characterization’ needs to be carried out to precisely control these particles in various heat transfer applications.

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