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2D-Based Nanofluids: Materials Evaluation and Performance

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Abstract

Advancement in technology demands the successful utilization of energy and its management in a greater extent. Thermal energy management plays a crucial role from high-payload electrical instruments to ultra-small electronic circuitries. The advent of nanofluids that happened in the 1990s successfully addressed the low thermal efficiency of conventional fluids in a significant manner. The ground-breaking report on the concept of “nanofluids for thermal management” led to the development of numerous thermal fluids using nanofillers of ceramics, metals, semiconductors, various carbon nanostructures, and composite materials. Later, demonstration of two-dimensional (2D) nanomaterials and their successful bulk synthesis led to the development of highly efficient fluids with even very low filler fractions. Introduction of 2D materials into fluids also brought out the multifunctional aspects of fluids by using them in tribology. In this chapter, we narrate the advances in thermal nanofluids and the development of novel fluids with the discovery graphene. Multifunctional aspects of these fluids are discussed here. To support the experimental observation, a theoretical platform is discussed and its predictions are correlated on the basis of existing data. The chapter has been concluded with a brief discussion on futuristic aspects of nanofluids in real-life applications. This chapter aims to focus on the description of the thermal transport, tribological behavior, and aspects that involve the use of 2D-based nanofluids, from various 2D nanostructures such as h-BN, MoS₂, WS₂, graphene, among others. The homogeneous nanoparticle distribution within conventional fluids and the results from the thermal transport and tribological tests and observations are included. The nanofluids under investigation belong mainly to dielectric and metal-mechanic lubricants. Also, the mechanisms that promote these effects on the improvement of nanofluids properties are considered.

Keywords: 2D nanostructures, nanofluids, tribology, wear, scuffing, thermal conductivity

1. General overview

Energy, the input to impulse the world's future, has been pointed out as the most important issue facing humanity in the next 50 years and crucial to solve issues like mitigation of pollution, global warming, among others [1]. For instance, among diverse forms of energy used, over 70% is produced in or through the form of heat [2]. Heat is transferred either to input energy into a system or to remove the energy produced in a system. Considering the rapid increase in energy demand worldwide, intensifying heat transfer process and thereby reducing energy loss are becoming increasingly important tasks. That is why thermal management plays a crucial factor concerning apparatuses or machines performance; thermal dissipation role has been subjected to many investigations and is under the scope of the operational useful life of these devices and components.

Nanotechnology is a science that deals with diverse phenomenon's, properties', and materials' characteristics at the nanometric level (1 nanometer, $\text{nm} = 10^{-9} \text{ m}$). Important and interesting discoveries have been realized in this field over the past 30 years. Among them, the discovery of Buckyball (C_{60}) [3], carbon nanotubes (CNTs) [4], and graphene isolation and identification [5] are just to mention some of them. During the last couple of decades, diverse techniques, equipment, and instrumentations have been devised, as well as various relevant and interesting characteristics and properties of these materials were sort out for the betterment of mankind.

Energy management becomes crucial for meeting the rising needs of mankind [2]. Nowadays, with increasing pressure of globalized markets and companies' profit race, a dramatic search is carried out for obtaining proper material performance; optimizing components and devices designs; improving efficiencies; reducing tools wear, materials consumption, and pollution; and obtaining the most possible revenue. In addition to issues regarding scrap materials, maintenance, and components wear among others, a hot topic in industry is the heat dissipation. Avoiding or reducing the use of resources for cooling equipment, or simply reflected in wear/friction issues among metal-mechanic processes, there is a high demand for successful heat management and energy-efficient fluid-based heat transfer systems, with aid of reinforced materials.

2. Introduction to nanofluids

Among diverse techniques to cool down or maintain certain temperature in these systems, vanes, fins, or radiators as well as forced air/fluids thru cooling channels are being used, even though they are costly. Some equipment and devices use inexpensive conventional heat transfer fluids to intensify heat dissipation, such as water (DiW), ethylene-glycol (EG), oils, and other lubricants. However, the inherent limitation of these fluids is the relatively low thermal conductivity; water, for instance, is roughly three orders of magnitude less conductive than copper or aluminum (**Table 1**). What these conventional fluids lack in thermal conductivity, however, is compensated by their ability to flow.

	Material	Thermal conductivity (W/m K)	Ref.
Conventional fluids	Water (DiW)	~0.598–0.609	[3, 10, 11]
	Ethylene glycol (EG)	~0.251	[12–14]
	Engine oil	~0.145	[12, 14]
	Mineral oil	~0.115	[15, 16]
	Kerosene	~0.139	[4]
	Toluene	~0.133	[4]
	R141b refrigerant	~0.089	[17]
Metallic solids	Aluminum	237	[18]
	Copper	398	[18]
	Gold	315	[18]
	Iron	80	[18]
	Nickel	91	[18]
	Silver	424	[18]
Carbon structures	Singlewall nanotubes (SWCNTs)	3000–6000	[19–22]
	Multiwall nanotubes (MWCNTs)	~3000	[23, 24]
	Carbon (diamond)	900–2320	[25, 26]
	Carbon (graphite)	119–165	[25]
	Graphene	~3000	[27, 28]
	Graphite	130–2000	[29]
Non-metallic solids	Alumina (Al ₂ O ₃)	31–41	[29–31]
	Aluminum nitride (AlN)	319–550	[32]
	Boron nitride (h-BN)	~300	[33, 34]
	Boron nitride nanotubes (BNNTs)	~600–960	[35–37]
	Boron nitride nanoribbons (BNNRs)	1700–2000	[42]
	Copper oxide (CuO)	76.5	[38]
	Molybdenum disulfide (MoS ₂)	34.5 ± 4	[39]
	Silicon carbide (SiC)	148	[18]
	Silicon oxide (SiO ₂)	1.4	[40, 41]
	Titania (TiO ₂)	8.4	[13]
	Tungsten disulfide (WS ₂)	32–53	[42]
	Zinc oxide (ZnO)	29	[13]

Table 1. Typical thermal conductivities for diverse conventional fluids and solid materials.

The primary mechanism for heat transfer in fluids is convection; its efficacy mostly depends on the thermo-physical properties of conventional fluids. Still, if the thermal conductivity of conventional fluids were enhanced, it would be much more effective. Hence, since the solid materials possess several orders higher thermal conductivity compared with that of conventional fluids, an idea to introduce conducting particles to fluids was considered. This idea occurred more than a century ago for Maxwell [6], where millimeter- or micrometer-sized solid particles were dispersed in conventional fluids to increase cooling rates, also a formulation of a method to calculate the effective conductivity of such suspensions was developed. Later, this technique was investigated and adapted for particle shape and composition by Hamilton and Crosser [7], but neither can predict the enhanced thermal conductivities of nanofluids (NFs) because their models do not include any dependence on particle size [8, 9]. Among diverse particle geometry, different particle shapes occur naturally or are engineered for specific applications (see **Figure 1**).

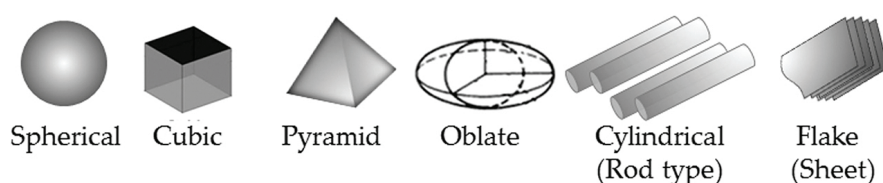


Figure 1. Diverse particle shapes and geometries.

Heat transfer using fluids is a very complicated phenomenon, and various factors such as fluid stability, composition, viscosity, surface charge, interface, and morphology of the dispersed particles influence the observed results [43–45]. Optimization and high efficiency of components and devices have gained great importance since these factors play a paramount role in diverse fields such as microelectronics, engine motors, fuel cells, air conditioning, power transmission systems, solar cells, medical therapy and diagnosis, biopharmaceuticals, components' and tools' wear, and nuclear reactors cooling, among others [15, 27, 46–49]. Solid materials such as metals, CNTs, oxide/nitride/carbide ceramics, semiconductors, and composite materials having higher thermal conductivity can be suspended within conventional fluids, resulting in better thermal transport performance composite fluids. Nevertheless, improvement in thermal conductivity cannot be achieved by just increasing the solid filler concentration because beyond a certain limit, increasing the filler fraction will also increase the viscosity, which will adversely affect the fluid properties and performance.

Most early studies used suspensions of millimeter- or micrometer-sized particles, which led to countless problems, such as a tendency to settle too rapidly, unless flow rate is increased; not only losing the enhancement in thermal conductivity but also forming sludge sediment, increasing the thermal resistance, and impairing the heat transfer capacity of the conventional fluids. In addition, increasing flow rate also increases erosion of pipelines or channels by the coarse and hard particles; outstanding thermal conductivity enhancement is based on high particle concentration, which leads to apparent increase in viscosity. Furthermore, fluids of this scale size could have considerably larger pressure drops, thus making flow through small

channels much more difficult since diverse parameters are critical for device performance, such as morphology and stability of dispersed particles or structures within these fluids, fluids composition, viscosity, fast sedimentation, channels clogging, wear or erosion, among others, which are often very serious for systems consisting of small channels [48–53]. Therefore, the search for nanofillers which can obtain high thermal conductivities at lower concentrations is desirable. Hence, extensive research has been done upon these conventional fluids, in order to develop improved materials to sublimely achieve all critical needs.

A revolution in the field of heat transfer fluids arose with the advent of NFs, a term introduced by Choi's research group in the late 1990s at Argonne National Lab (ANL) [52]. First research was conducted by Masuda et al. [53] for $\gamma\text{-Al}_2\text{O}_3$ particles in water, and by Choi-Eastman group [52] for Cu in water as well. As depicted by **Figure 2**, nanofluids research has been increasing through time, reaching up to 1100 publications in 2015, according to scientific search engine "sciencedirect.com" and keyword *Nanofluid*. On the inset of **Figure 2**, two keywords were applied *Nanofluid* and *2D*, where nearly 150 publications in 2015. Nanofluids are a new class of stable heat transfer liquid suspensions which are engineered containing homogeneously dispersed solid nanofillers (ultra-fine particles, fibers rods, or tubes <100 nm). Compared to micro- or milli-fluids, nanofluids tend to be more stable, since nanofillers possess unique properties, such as large surface area to volume ratio, as well as dimension-dependent physical properties, which make nanostructures better and more stably dispersed within conventional fluids. Nevertheless, some limitations of the effective incorporation of nanoparticles within conventional fluids are dispersion and solubility because these tend to aggregate and settle. In some cases, additives or surfactants are used to stabilize the nanoparticles within the fluids, even though the surfactants can decrease the thermal conductivity of the nanofluids, since surfactants introduce defects at the interfaces [54].

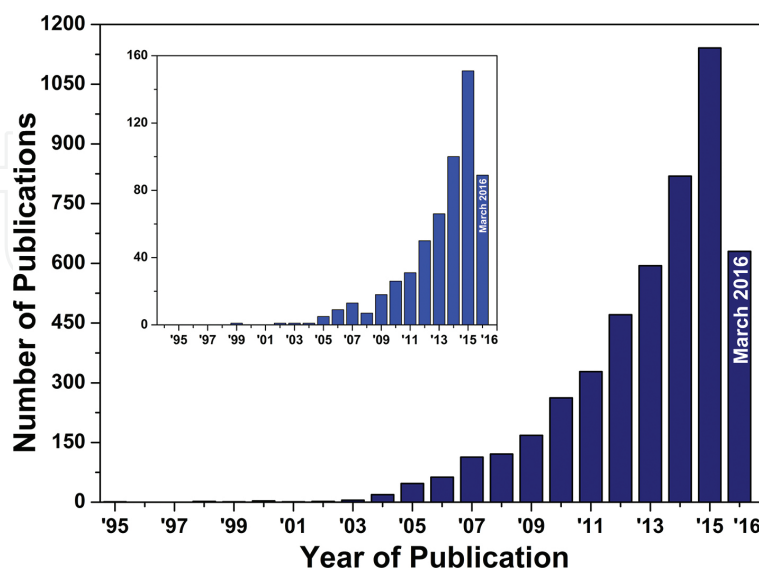


Figure 2. Number of publications with "Nanofluid" as search topic, according to Scienedirect.com; inset showing number of publications with keywords "Nanofluid" and "2D."

Therefore, one of the main advantages of nanofluids is that they can be specially engineered to optimally fulfill particular objectives, such as enhanced thermal conductivity, a higher thermal energy storage capacity, a higher heat transfer coefficients, a better temperature stabilization, and less pressure drop, among others. Moreover, nanofluids are promising for practical application without clogging, sediment or such. Nanofluids will keep the fluidic properties of the conventional fluids, behave almost like conventional fluids, and incur in little or no extra penalty of pressure drop (i.e., the viscosity increase is small) due to the fact that dispersed nanoparticles are extremely small, which are very stably suspended in fluids with or without the aid of additives or surfactants [55]. Hence, search for new nanofillers which can get high thermal conductivities at lower filler fractions is important [15, 56].

It has been demonstrated that nanofluids for heat transfer applications have provided better thermal performance than conventional fluids [12, 15, 48, 49, 56–58]. Therefore, the advent of nanofluid-based heat transfer systems can make compact designs with highly efficient thermal, physical, and electrical performance for instruments and devices.

Experiments on convection heat transfer of nanofluids were conducted by several research groups [57, 59–61]. The results showed significant improvements in heat transfer rates of nanofluids. Meanwhile, the thermal conductivity enhancement of nanofluids shows a temperature-dependent characteristic—increase of enhancement with rising temperature, which makes the nanofluids more suitable for applications at elevated temperatures [15, 49, 62–66]. Additionally, previous research has shown that nanofluids display better performance in their thermo-physical and tribology properties, such as thermal conductivity, thermal diffusivity, viscosity, friction, etc., compared to conventional fluids [15, 46–49, 67–71]. Hence, nanofluids could be used for aforesaid engineering applications. From all these, a great variety of nanocomposite materials have been developed, using diverse techniques and methodologies, obtaining significant performance.

3. Synthesis and preparation of nanofluids

The manipulation of matter on the nanometer scale has become a central focus from both fundamental and technological perspectives. Unique, unpredictable, and highly intriguing physical, mechanical, optical, electrical, and magnetic phenomena result from the confinement of matter into nanoscale features. Morphology control in nanostructures has become a key issue in the preparation of electronic or mechanical nanodevices and functional materials [72]. A wide variety of combinations of nanostructures and conventional fluids can be used to synthesize and prepare stable nanofluids for diverse applications. Nanofluids could be manufactured by two methods:

- (a) *One-step method*: The one-step process simultaneously makes and disperses the nanostructures within the base fluid. This method avoids diverse processes such as particles drying, storage, handling, and dispersion, so the agglomeration of nanoparticles is minimized; therefore, stability of nanofluids is improved [73]. Thus, it is possible to obtain

uniformly dispersed and highly stable suspended nanostructures within the base fluids [74, 75].

- (b) *Two-step method*: Two-step method is the most widely used method for preparing nanofluids [15, 49, 76–82]. Various nanostructures such as nanofibers, nanotubes, nanosheets, among other nanomaterials used in this technique are initially produced by mechanical comminuting, chemical reaction, vapor condensation, or decomposition of organic complex [83–85] and finally obtained as dry powder. Then, it is followed by further dispersion of as-produced nanostructures within base fluids through magnetic force agitation (stirring), ball milling, ultrasonic agitation, and high-shear mixing, among others [77, 81, 86, 87]. This procedure is the most economic method to produce nanofluids in large scale since nanoparticle synthesis techniques are readily scaled up to mass production levels. Sonication is used to speed dissolution by breaking intermolecular interactions, and homogeneously dispersing nanoparticles within a fluid. It is especially useful when it is not possible or difficult to stir a sample.

3.1. Nanofluids: variables and features

Diverse features and challenges regarding the effect of nanoparticles on thermal transport, tribological performance, and energetic performance have been studied. The heat transfer enhancement in nanofluids, for example, has been attributed to many variables including nanoparticle size, shape, and filler fraction. However, as mentioned, diverse challenges have hindered their large-scale applications (**Figure 3**), such as nanoparticle dispersion, agglomeration, long-term stability, increase in nanofluid viscosity, cost increase, and scale-up capacity for industrial applications, which are presented in the following sections.

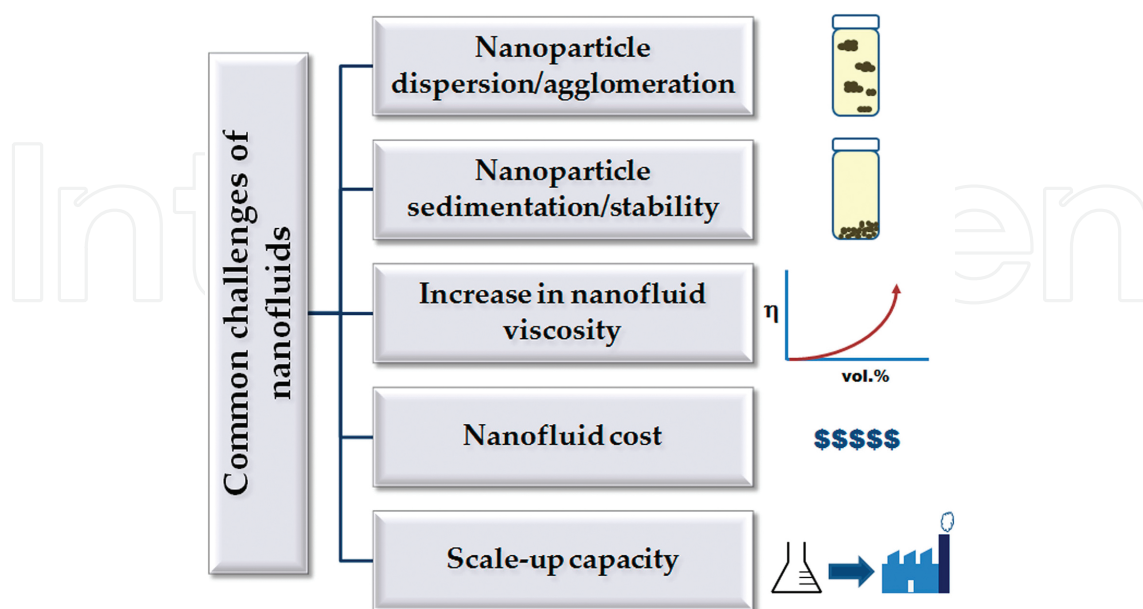


Figure 3. Common challenges of nanofluid developments.

3.1.1. Nanofiller size

Diverse studies have found that as nanoparticles are reduced in size, the effective thermal conductivity of the nanofluid increases [13, 64, 88–94]. As the nanoparticle size is reduced, Brownian motion is induced. Also, lighter and smaller nanoparticles are better at resisting sedimentation, one of the biggest technical challenges in experimenting with nanofluids [61]. Li et al. [88] investigated the thermal properties of $\text{Al}_2\text{O}_3/\text{DiW}$ nanofluids with particle sizes of 36 and 47 nm at various filler fractions. The nanofluid with 36-nm particles improved the effective thermal conductivity enhancement at $\sim 35^\circ\text{C}$, varying the filler fractions from 0.5 to 6.0 vol.% (~ 7 to $\sim 28\%$, respectively). Similar trend was observed for the nanofluid with 47 nm particles, but slightly lower thermal conductivity enhancement was shown compared to the smaller particles nanofluid (~ 4 to $\sim 25\%$, respectively). Nguyen et al. [95] and Minsta et al. [89] studied the heat transfer enhancement and behavior of Al_2O_3 -water nanofluid for microprocessors/electronic purposes. It is found that with smaller nanoparticles (36 nm in diameter), nanofluids showed higher convective heat transfer coefficients than with larger ones (47 nm in diameter). From Nguyen's research, thermal transport increased 40% at 6.8 vol.% filler fraction, as compared to water. Chopkar et al. [96] studied 0.20–2.0 vol.% $\text{Al}_{70}\text{Cu}_{30}$ nanoparticle reinforced EG, and also found that thermal conductivity strongly depends on the size of nanoparticles.

He et al. [97] studied the heat transfer behavior of TiO_2 -water nanofluids with diameters of 95, 145, and 210 nm at various filler fractions. For the 95-nm-particle-size nanofluid, the thermal conductivity showed an increase from 1 to $\sim 5\%$ at 1.0 and 4.9 wt.%, respectively, compared to water; as filler fraction increased, the thermal conductivity increased as well. It was shown that the effective thermal conductivity decreases as particle size increases. Research conducted by Hong et al. [77] achieved 18% increase in thermal conductivity with only 0.55 vol.% of Fe-nanoparticles (~ 10 nm size)-reinforced EG nanofluids. Showing as well that sonication of the nanofluid has an important effect on the thermal conductivity of the system indirectly proves the effect of particle size on the thermal conductivity of the nanofluid. Teng et al. [92] studied the effect of particle size, temperature, and weight fraction on the thermal conductivity ratio of Al_2O_3 /water nanofluid with filler fraction up to 2.0 wt.%, and different Al_2O_3 particle nominal diameters (20, 50, and 100 nm). The results showed a dependence relationship between high thermal conductivity ratios and enhanced sensitivity, small nanoparticle size, and higher temperature. Hence, nanofillers' size is a determinant variable for heat transfer nanofluids, since, as previously stated, its smaller size reduces or avoids critical issues of larger fillers.

Nevertheless, there have been a few reports on SiC, CeO_2 , and Al_2O_3 nanoparticles reinforcing water that stated a decrease of the effective thermal conductivity with increase in particle size [98–101]. As shown by Beck et al.'s [100] research on Al_2O_3 /water nanofluids with diverse particle sizes ranging from 8 to ~ 300 nm in diameter, the thermal conductivity enhancement decreases as the particle size decreases below ~ 50 nm. Beck et al. attribute this behavior to nanoparticles thermal conductivity, as the particle size becomes small enough to be affected by increased phonon scattering [100]. Similarly, studies performed on water-based CeO_2

nanofluids [101] showed an increase in the effective thermal conductivity with an increase of nanoparticle size, although only two particle sizes were studied (12 and 74 nm).

3.1.2. Particle shape/surface area

Several studies have found that rod-shaped nanoparticles, such as CNTs, remove more heat than spherical nanoparticles [78, 102–107], probably because rod-shaped particles have a larger aspect ratio (the ratio between a particle's surface area to volume) than spherical nanoparticles. Elias et al. [103] studied various boehmite alumina (γ -AlOOH) nanoparticle shapes (cylindrical, spherical, bricks, blades, and platelets) within EG/water (50/50%). Nanofluids at diverse filler fraction, up to 1.0 vol.%, showed a linear increase in thermal conductivity. Best performance was found for cylindrical-shaped nanoparticles, followed by bricks, blades, platelets, and spherical-shaped nanoparticles, respectively. Thermal conductivity enhancement of cylindrical-shaped nanoparticles is observed to be $\sim 2.5\%$ higher than the spherical shape with 1.0 vol. % filler fraction. Murshed et al. [104] investigated water reinforced with TiO₂ rod-type (10 nm in diameter and 40 nm in length) and spherical (15 nm) nanoparticles; an enhancement of thermal conductivity of ~ 30 and $\sim 33\%$, respectively, was observed at 5.0 vol.% filler fraction compared to base fluid. EG-based nanofluids with addition of SiC nanowhiskers (1.5 μm in diameter and 18 μm in length) and spherical particles (diameter $< 40 \mu\text{m}$) were investigated by Cherkasova et al. [106]. Nanowhiskers were prepared at various aspect ratios by ball milling from 0, 4, 12, and up to 28 h. At 2.5 vol.%, the thermal conductivity enhancement is observed to increase from 16.5 to 39.5% as the aspect ratio increases from 4.8 to 9.6. It is also observed that suspensions containing cylindrical particles showed significantly higher increase in thermal conductivity than suspensions with dispersed spherical particles. For 5.0 vol.%, a thermal conductivity enhancement of ~ 85 and $\sim 20\%$ was observed for suspensions containing SiC whiskers and spheres, respectively. Thermal conductivity increase for both types of particles is nearly linear with volume fraction of solids up to 5.0 vol.% as well. On other research on rod-type nanoparticles, Glory et al. [105] studied multiwall nanotubes (MWCNTs)/water nanofluids. An increase in thermal conductivity enhancement was observed with an increase of nanotube length. For instance, the relative increase of thermal conductivity of nanofluids at 2.0 wt.% with nanotubes with length of $\sim 0.5 \mu\text{m}$ was $\sim 14\%$, an 18% increase was observed for nanotubes with length of 1.0 μm , a 38% increase was observed for nanotubes with length of 1.7 μm , and finally, a $\sim 45\%$ increase was observed for the longest nanotubes tested with length of $\sim 5.0 \mu\text{m}$. As explained by Glory et al., this behavior is attributed to a mechanism where longer nanotubes diminish the number of nanotube-nanotube contacts, therefore favoring phonon transmission in the suspensions, giving an increase of the thermal conductivity. Other nanoparticles with morphology possessing large surface area are the 2D nanosheets, which are obtained by exfoliation layers in its structure [15, 108]. Moreover, little research has been conducted for 2D-nanoparticles reinforcing conventional fluids. Recently, it has been demonstrated by Taha-Tijerina et al. [15, 49] that 2D-based nanofluids have high impact in the thermal transport, as well as in physical, electrical, and tribological properties.

3.1.3. Filler fraction

Probably, the key variable for nanofluids' improvement is the nanofillers concentration homogeneously dispersed within conventional fluids. Filler fraction has been stated by volume and weight percentages in papers, patents, and reports. Effective thermal conductivity (k_{eff}) and coefficient of friction (COF), among other properties of nanofluids improve with increasing nanoparticles filler fraction [109], but as the nanoparticles filler fraction increases, it may no longer be valid to assume a well-suspended nanoparticles. Also, pressure drop has been observed in diverse conventional fluids as filler fraction of different nanoparticles is increased [10]. This is why it is more effective to use a very small filler fraction in nanofluids [15, 110–113]. At low filler fractions, nanostructures have more intense Brownian motion at higher temperatures, which can significantly enhance the effective thermal conductivity. But at high volume fractions, nanoparticles have high potential to be agglomerated at high temperatures.

3.1.4. Particles agglomeration

A key challenge with nanofluids is that nanoparticles tend to agglomerate due to molecular interactions, such as Van der Waals forces [99, 114]. Agglomeration of nanoparticles increases as filler fraction increases, due to closer particles and higher Van der Waals attraction. Similarly, this issue generates other problems such as viscosity increments (**Figure 4**). Agglomeration causes the effective surface area to volume ratio to decrease, which impacts the thermal conductivity performance of the fluid. Timofeeva et al. [99, 107] studied the thermal conductivity and viscosity of Al_2O_3 nanoparticles dispersed in water and EG. It is observed that the main parameters for controlling nanofluids' thermal conductivity enhancement are the geometry, agglomeration state, and surface resistance of nanoparticles. Karthikeyan et al. [109] identified that CuO nanoparticles and cluster size have a significant influence on thermal conductivity of water and EG. Similarly, it is found that nanoparticle agglomeration is time dependent; as time elapsed, agglomeration increased, which decreased the thermal conductivity. Wang et al. [115] performed studies on diverse fluids (water, pump fluid, engine oil, and EG) with the addition of Al_2O_3 and CuO with 28 and 23 nm in diameter, respectively. Viscosity of these systems increase as nanoparticles agglomerate, also thermal conductivity performance is observed to decrease, most probably an effect of the agglomeration of the nanoparticles. Moreover, particle agglomeration is exacerbated by the size of the reinforced fillers. Nasiri et al. observed a reduction in thermal conductivity with time for water-based CNT nanofluids due to agglomeration [114]. However, some reports show that aggregation in water-based Al_2O_3 nanofluids significantly increases the thermal conductivity of the fluid [116, 117]. In other studies, stable nanofluids showed no significant variation in thermal conductivity with time. Yu et al. observed that the thermal conductivity of EG-based ZnO nanofluids [118] and kerosene-based Fe_3O_4 nanofluids [119] were independent of time. Additionally, engine coolant-based Al_2O_3 nanofluid exhibited minimum change of thermal conductivity with time [120]. Yu et al. [121] conducted studies on EG-based graphene oxide nanosheets (GON). An enhancement in thermal conductivity at 5.0 vol.% of $\sim 61\%$ was observed. Thermal conductivity performance was invariable for ~ 7 days, reflecting high stability of GON/EG nanofluids.

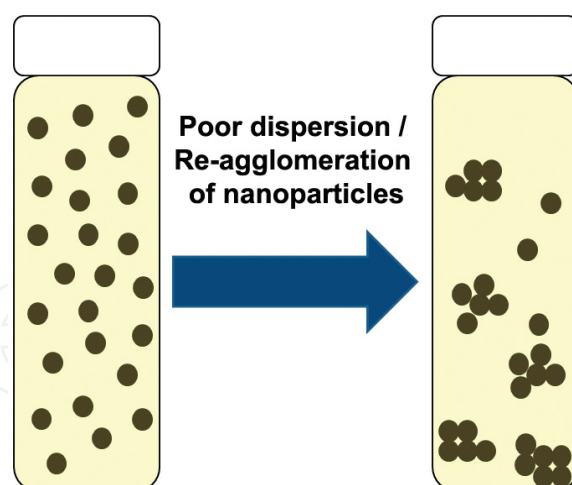


Figure 4. Scheme of nanoparticles sedimentation over time.

3.1.5. Stability

Because the reinforced particles are so small, weight is less, and the sedimentation probability is less too (**Figure 5**). This reduced nanostructures sedimentation can overcome one of the major drawbacks of suspensions, the settling of particles, and make the nanofluids more stable. In some cases, to enhance the stability of the nanofluids, surfactants or additives are used; nevertheless, there are certain drawbacks of using them.

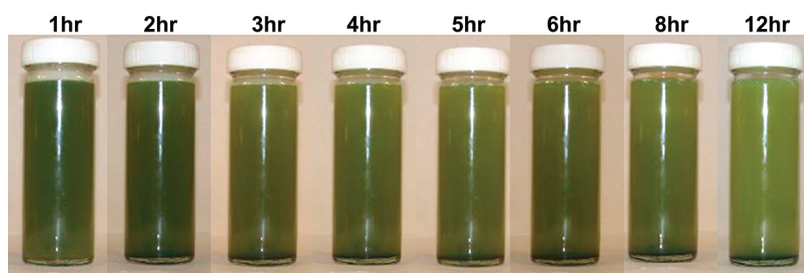


Figure 5. Nanoparticles sedimentation; CuO-reinforced nanofluids over time.

3.1.6. Surfactants/additives

Surfactants are mainly used to stabilize the nanofillers within the conventional fluids, even though these surfactants can affect the nanofluids performance, since surfactants introduce defects at the molecular interfaces [54]. The use of surfactants and dispersion agents has shown to be effective providing repulsion between nanoparticles and reducing agglomeration [49, 81, 122, 123]. Additives are also incorporated to materials to enhance their mechanical properties. For instance, Chen et al. [124] found that the addition of stearic acid (SA) coated MWNTs, and performed as lubricant, improving the friction reduction and anti-wear properties of MWNTs. Non-ionic surfactants were found to strongly interact with graphite surfaces in case of CNTs

stabilization within aqueous suspensions [125]. Wang et al. [126] investigated oil with addition of graphite nanoparticles ($\sim 10\text{--}30\text{ nm}$), and also using a dispersant (CH-5) up to 12.0 wt.%. Graphite nanofluids at various filler fractions, from 0.5 to 4.0 wt.%, showed an increase in thermal conductivity from 0.5 to 20%, respectively. These increments were improved with the addition of dispersant (1.5–12.0 wt.%) from 2.4 to 36%. According to Wang et al., this behavior is due to the improvement in dispersibility of graphite with the aid of the dispersant. Oleic acid (OA)-modified TiO_2 nanostructures increased the maximum non-seizure load 6–10 times when added to water [127]. Recently, OA was added to h-BN/mineral oil nanofluids [49] showing a decrease of 8 and 3% COF and wear scar diameter (WSD), respectively, compared to the surfactant-less material. Similarly, the addition of OA surfactant in nanolubricants of CuO and MoS_2 in palm oil facilitated the reduction of agglomerates, thus improving the tribological properties [123]. In other cases, nanoparticles are used as additives to enhance their useful life, as well as antimicrobial agents. In metal-mechanic industry, for instance, diverse fluids are used to cut or lubricate stamping or metal-cutting processes. Nevertheless, some of them provide a breeding ground for large numbers of microorganisms (fungi/bacteria) which is hazardous to the machine operators [128, 129]. Kumar et al. used silver (Ag) nanoparticles dispersed in paints based on vegetable oil [130], since silver is highly antimicrobial by virtue of its antiseptic properties against several kinds of bacteria, fungi, and viruses [130, 131].

3.1.7. Viscosity

Viscosity is described as the internal resistance of a fluid to flow. Viscosities in nanofluids are dependent on both fillers geometry and surface properties of nanofillers. As mentioned by Timofeeva et al. [107], elongated particles and agglomerates result in higher viscosity at the same filler fraction due to structural limitation of rotational and transitional Brownian motions. Nguyen et al. [132] have investigated on particle size effect for Al_2O_3 aqueous-based nanofluids and observed that the particle size effects on viscosity are more significant for high particles concentration. Taha-Tijerina et al. [15] investigated mineral oil reinforced with 2D nanostructures of h-BN and graphene at very low filler fractions. It was observed that the viscosity of the nanofluids decreases significantly with temperature (from $16\text{ mm}^2/\text{s}$ at room temperature to $2.2\text{ mm}^2/\text{s}$ at 100°C), as expected; while the enhancement in viscosity with the addition of 2D-nanofillers is very small ($<2\%$ at 313 K). This is an additional advantage of the low filler fractions since the increase in viscosity will decrease the effective thermal conductivity values as well as flow characteristics of the fluid. Moreover, the relatively small increase in viscosity ($<30\%$) at 0.35 wt.% of h-BN is an evidence that the solution is not flocculating [133, 134]. Small deviations from the theoretical values of viscosity at higher concentrations of h-BN/MO may be as a result of a transition from a dilute to a semi-dilute phase or due to the onset of some small aggregation between the h-BN nanosheets [15].

3.1.8. Brownian motion

Researchers have found that Brownian motion, which is the random movement of particles (**Figure 6**), is one of the key heat transfer mechanisms in nanofluids [62, 115, 135–140]. Keblinski et al. stated possible micro-mechanisms for nanofluids thermal conductivity increase, among

which Brownian motion was the reason for this [45]. Moreover, Jang et al. proposed that particles' Brownian motion can induce nanoscale convection, which enhances the thermal conductivity of nanofluids [135]. Brownian motion only exists when the particles in the fluid are extremely small, and as the size of the particles gets larger, Brownian motion effects diminish [61].

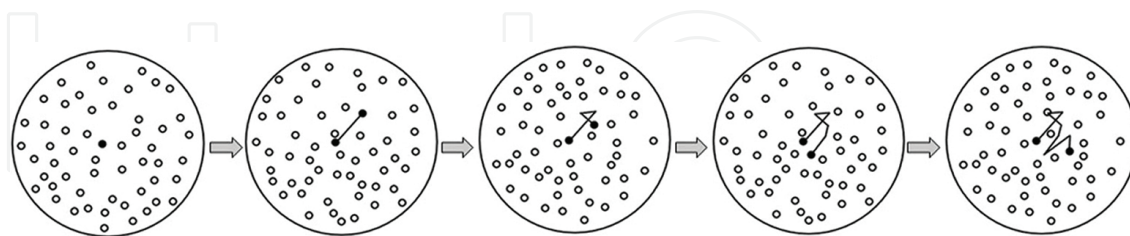


Figure 6. Representative scheme of Brownian (random) motion of nanoparticles.

3.1.9. Temperature dependence

Nanofluids' effective thermal conductivity and Brownian motion increase with temperature [11, 61–65, 141–143]. Das et al. [62], similarly to Lee et al. [144], observed that Al_2O_3 and CuO nanofluids thermal conductivity has temperature-dependent influence (in the range from 20 to 50°C); they posed motion of reinforced fillers as an important factor for that. Hu et al. showed a 20% increase in the thermal conductivity of ethanol with the addition of 4.0 vol.% of AlN at 273 K, and a strong temperature dependence of the thermal conductivity [145]. Similarly, Yu et al. [146] research on Al-N nanofluid showed an enhancement of $\sim 40\%$ with a little effect on temperature from 10 to 60°C . Wang et al. [40] measured thermal conductivity of TiO_2 (26 nm) and SiO_2 (23 nm) nanoparticles suspended in DiW, EG, and ethanol. The experiment was conducted with 1.0–4.0 vol.% filler fractions at temperatures ranging from 18 to 65°C . Results indicated that thermal conductivity of nanofluids was higher than the base fluids and increased with rise of temperature and filler fraction. For instance, from measurements taken at 18– 65°C , TiO_2/DiW nanofluid thermal conductivity improved from 3, 4, and 10% to 9, 10, and $\sim 20\%$ at filler fractions of 1.0, 2.0, and 4.0 vol.%, respectively. As seen from research conducted by Wen et al. [66], the effective thermal conductivity increases with increasing temperature, showing a non-linear dependence after temperatures above $\sim 30^\circ\text{C}$. On the other hand, studies by Das et al. [147] on $\text{Al}_2\text{O}_3/\text{water}$ nanofluids have shown that the thermal-conductivity ratio increased with temperature in a linear fashion.

Jyothirmayee et al. [141] observed a temperature dependence on graphene nanosheets (GnS)-reinforced EG and DiW, on temperatures ranging from 25 to 50°C . It was observed that the thermal conductivity increases with increasing graphene concentration and temperature. The thermal conductivity of the base fluids did not show much enhancement as the temperature increases, similar tendency as reported by Jha et al. [148]. An enhancement in thermal conductivity of $\sim 2.4\%$ is observed at 25°C with a very low filler fraction of 0.008 vol.% of the graphene/EG nanofluid, meanwhile, at 50°C , this increases to $\sim 17\%$. At 0.14 vol.%, the enhancement in thermal conductivity is 6.5% and 36% at 25 and 50°C , respectively. The behavior is similar as reported by Chon et al. [64] and Xie et al. [149]. For the 0.14 vol.%

graphene/DiW nanofluid, the enhancement is about 13.6% and 94.3% at 25 and 50°C, respectively. These high increments in thermal conductivity exhibited by the graphene-based nanofluids can be ascribed to the high aspect ratio of defect-free graphene sheets. Walvekar et al. [150] and Ding et al. [151] performed diverse studies on CNTs-water nanofluids, showing that thermal conductivity is highly dependent on temperature as well.

3.1.10. Interfacial layering on the liquid-nanostructure interface

Interfaces are ideal templates for assembling nanoparticles into 2D structures by the nature of the interfaces. At the interfaces, the nanoparticles are mobile and defects of the structures can be eliminated [152]. This ordered structure could have higher thermal conductivity than that of the conventional, therefore an enhancement of the effective thermal conductivity. However, some issues could be addressed when a surfactant or dispersant is used [66]. Interfacial layering refers to a phenomenon at the liquid–particle interface where liquid molecules are more ordered than those in the conventional liquid; therefore the interface effect could enhance the thermal conductivity by the layering of the liquid at the solid interface (giving that crystalline solids possess much better thermal transport than liquids) [45, 153], by which the atomic structure of the liquid layer is significantly more ordered than that of the conventional liquid. Various researchers have suggested that there is a liquid layering on the nanoparticles, which helps enhance the heat transfer properties of the nanofluid [151, 154–156]. Yu et al. [156] proved the formation of layers by the liquid molecules close to a solid surface, even though the thickness and thermal conductivity of the nanolayers are not well known yet. Ren et al. [157] found, through a theoretical model, that adding liquid layering on the nanoparticles an increase in layer thickness leads to higher thermal conductivity increment; as larger the size of the suspended particles, the weaker appear the effects of the nanolayer and the thermal motion.

4. Nanofluids application fields

Diverse studies on nanofluids have been carried out by many researchers. This section deals with literature reviews on nanofluids; nanofluids preparation and characterization; thermo-physical, electrical, and tribological properties; as well as nanofluids applications, which lays foundation and basis for further investigations. Some of the main fields of application for these systems are thermal management and tribological, which are described in the following sections.

4.1. Thermal performance of nanofluids

Heat transfer is classified into various mechanisms, such as thermal convection, thermal radiation, and thermal conduction. In diverse fields, thermal transport is a critical parameter to obtain efficient performance of components and devices. Heat convection occurs when bulk flow of a fluid (gas or liquid) carries heat along with the flow of matter in the fluid, this process could be “natural,” by density differences in the fluid occurring due to temperature gradients, or “forced,” where fluid motion is generated by an external source such as a pump, fan, or

other mechanical means. Radiation heat transfer is the transfer of energy by means of photons in electromagnetic waves in much the same way as electromagnetic light waves transfer light. On the other hand, heat conduction is the direct microscopic exchange of kinetic energy of particles through the boundary between two systems. When an object is at a different temperature from another body or its surroundings, heat flows so that the body and the surroundings reach the same temperature, at which point they are in thermal equilibrium. The thermal conductivity (k) of liquids can be successfully measured if the time taken to measure k is very small so that the convection current does not develop [158]. Effective thermal conductivity (k_{eff}) is described as the nanofluid thermal conductivity, compared to conventional fluid thermal conductivity. Diverse techniques have been proposed to measure nanofluids thermal conductivity over the past years. The most common techniques to measure the effective thermal conductivity of nanofluids are the transient hot-wire method [15, 47, 99, 126, 158–161], steady-state method [35, 88, 105, 115, 162], cylindrical cell method [163], temperature oscillation method [62, 164–166], and $3\text{-}\omega$ method [40, 167–169] to name a few.

Heat transfer fluids have been explored in diverse systems. Argonne National Lab research group with Eastman et al. reported a 40% enhancement with only 0.40 vol.% of copper oxide (CuO) particles of 10 nm in diameter [83], while Choi et al. reported a remarkable 160% increase in thermal conductivity of MWCNTs/engine oil nanofluid at 1.0 vol.% filler fraction of nanotubes [170]. Marquis et al. [19] reported a thermal conductivity enhancement of 45% at 1.0 vol.% concentration of highly pure SWCNTs in 15W-40 oil. In this same investigation, a remarkable enhancement of 175% with 1.0 vol.% of MWCNTs in poly- α -olefin (BP Amoco Ds-166) oil is obtained, similar to Choi found at 1.0 vol.% of nanotubes in oil [170]. Similarly,, other researchers have investigated the effect of CNTs in diverse fluids with aid of dispersants. For instance, Liu et al. [14] measured the thermal conductivities of nanofluids containing MWCNTs dispersed in EG and synthetic engine oil. The increase of thermal conductivity for MWCNT/EG at 1.0 vol% was $\sim 12.5\%$, meanwhile, for MWCNT/synthetic engine oil, an improvement of ~ 9 and 30% for 1.0 and 2.0 vol.% filler fraction was observed. Wen et al. [66] investigated the effect of temperature on the thermal conductivity of MWCNTs/DiW (20–60 nm in diameter and micrometer size in length) nanofluids. In order to properly stabilize the MWCNTs within DiW, 20 wt.% of sodium dodecyl benzene sulfonate (SDBS) was added to all samples. At 0.84 vol.% filler fraction, thermal conductivity enhancements of ~ 24 and $\sim 31\%$ were achieved at 20 and 45°C , respectively. In general, an improvement on thermal conductivity enhancement was observed as filler fraction and temperature increased. Assael et al. [78] studied the MWCNTs/DiW nanofluids with addition of 0.10 wt.% sodium dodecyl sulfate (SDS) as a dispersant. According to Assael et al., SDS would interact with MWCNTs, affecting their outer surface, enhancing interactions with DiW. It was found that at 0.60 vol.% MWCNTs, the enhancement in thermal conductivity was $\sim 38\%$. Hwang et al. [41] investigated the thermal conductivity of DiW- and EG-based nanofluids. MWCNTs (10–30 nm in diameter and 10–50 μm in length), CuO, and SiO_2 (33 and 12 nm in diameter, respectively) were used. It was observed that thermal conductivity of nanofluids was improved almost linearly as filler fraction increased. For DiW-based systems, the addition of SiO_2 , CuO, and MWCNTs at 1.0 vol.% filler fraction showed an increase of 3, 5, and $\sim 12\%$, respectively. Also, CuO/EG nanofluid at 1.0 vol.% showed an increase of $\sim 9\%$.

Ding et al. [66] also investigated the effects of MWCNTs dispersed in DiW, with addition of 0.25 wt.% gum Arabic (GA) dispersant. For MWCNTs at 0.50 and 1.0 wt.%, an increase in thermal conductivity was achieved up to ~ 30 and $\sim 38\%$ at 25°C , and ~ 35 and $\sim 80\%$ at 30°C , respectively. It was found that these improvements were slightly higher than that results reported by Liu et al. [14], Wen et al. [151], Assael et al. [78], and Xie et al. [171], but lower than that showed by Choi et al. [170]. There are diverse factors that cause these discrepancies among the different groups; as mentioned by Wang et al. [138], these discrepancies should rely on the dependency of thermal conductivity is on diverse factors such as the structure and properties of the CNTs, aspect ratio, clustering, addition of dispersants, temperature and the experimental errors as well. Hong et al. [58] successfully developed stable and homogeneous nanolubricants and nanogreases based on CNTs in polyolefin oils. Thermal conductivity experiments showed an increment of 20% at 0.10 wt.% filler fraction; similarly, at 3.0 and 10 wt.%, thermal conductivity increments were 50 and 80%, respectively. More recently, Walvekar et al. [150] analyzed the effect of CNTs on diverse temperatures ranging from 25 to 60°C . CNTs/DiW nanofluids were stabilized with the addition of GA as dispersant. Superb results showed improvements at diverse filler fractions, varying from 0.01 to 0.10 wt.%, and diverse temperatures, ranging from 25 to 60°C . A maximum thermal conductivity enhancement of $\sim 288\%$ was shown for 1.0 wt.% CNTs/DiW nanofluids at 60°C .

Research on oxide nanoparticles have been conducted as well. Das et al. [62], for instance, showed strong temperature dependence of nanofluids with Al_2O_3 and CuO particles as used by Lee et al. [144], which significantly improved the scope of nanofluids as an alternate for existing coolants. In 2005, Chon et al. [64] and Li et al. [172] confirmed this, but no temperature effect on thermal conductivity enhancement of nanofluids was observed in CNTs [173]. Li et al. [174] synthesized kerosene-based nanofluids with dispersed Cu nanoparticles (~ 40 – 60 nm in diameter). Temperature dependence on thermal conductivity for Cu/kerosene-based nanofluids showed that as nanofluid temperature increases, thermal conductivities increased as well. For measurements at 25, 40, and 50°C , the effective thermal conductivity increased by ~ 10 , ~ 13 , and 15%, respectively, with 1.0 wt.% Cu nanoparticles. In other investigations, nanodiamonds (<10 nm) dispersed in EG (with addition of poly (glycidol) polymer) and MO (with addition of OA) were studied by Branson et al. [175]. It was observed that addition of 0.88 vol.% of nanodiamonds enhanced the thermal conductivity by $\sim 12\%$. In MO, for instance, with enhancements of ~ 6 and $\sim 11\%$, filler fractions of 1.0 and 1.9 vol.% are achieved, respectively. According to Branson et al., the differences on enhancement efficiencies are attributable to divergence in thermal boundary resistance at nanoparticle/surfactant interfaces [175].

Several research studies have developed graphene-based nanofluids with high nanoparticle stability and significant enhancements [146, 176–183]. Shaikh et al. studied the effect of exfoliated graphite (2D sheets in micrometer size range) dispersed within poly- α -olefin (PAO) oil at various filler fractions, ranging from 0.10 to 1.0 vol.%. It was observed that addition of 2D structures improved the thermal conductivity from 18 to $\sim 130\%$, respectively [176]. Moreover, Yu et al. [180] investigated EG/graphene sheets (0.20– $2.0\ \mu\text{m}$ range, and 0.43 nm of interplanar distance), obtaining up to $\sim 86\%$ increase in thermal conductivity with 5.0 vol.% concentration at 50°C . Hadadian et al. [184] prepared highly stable graphene oxide (GO)-based

nanosheets. Thermal transport of EG increased by 30% with 0.07 GO mass fraction. Other EG-based nanofluids synthesized by Yu et al. [121, 180] have shown better enhancements of 61 and 86% with graphene oxide [121] and graphene nanosheets [180], respectively, at 5.0 vol.% loading. Similarly, a different study by Yu et al. [146] with graphene oxide nanosheets found enhancements of up to 30.2, 62.3, and 76.8% for distilled water, propyl glycol, and liquid paraffin (LP), respectively. Kole et al. [159] obtained a 15% in thermal conductivity with 0.395 vol.% exfoliated GnS dispersed in distilled water. Moreover, Aravind et al. [178] synthesized graphene and graphene-MWCNT composite nanoparticles and dispersed them in polar base fluids. Enhancements in thermal conductivity of de-ionized water of 9.2 and 10.5% were found for graphene and graphene-MWCNT, respectively. According to this study, a synergistic effect was found for graphene-MWNT additives; furthermore, MWNTs prevented restacking of graphene sheets.

Diverse theories explain the mechanisms that could affect the behavior of nanofluids; the most accepted being Brownian motion [40, 137–140], percolation theory [137, 138, 154, 173, 185], micro-convection cell model [137–140, 154, 185], and liquid layering theory [45, 137, 138, 153, 154, 185]. **Table 2** shows the influence of oil-based nanofluids on thermal conductivity. Similarly, **Table 3** shows the results from diverse investigations on other water-based nanofluids, and various materials and sizes used as reinforced nanoparticles. **Table 4** shows the influence of various nanofluids in thermal management properties, as well.

Filler	Type of oil	Nanoparticles morphology	Filler fraction	TC enhancement	Ref.
Al_2O_3	Engine oil (10W-30)	Spherical ~28 nm diam.	5.0 vol.% 7.5 vol.%	~26% ~30%	[115]
Al_2O_3	Engine oil	Spherical ~80 nm diam.	0.5 vol.% 1.0 vol.%	~9% ~12%	[186]
Al_2O_3	Mineral oil	Spherical ~13 nm diam.	4.0 vol.%	>20%	[187]
Al_2O_3	Pump oil	Spherical ~28 nm diam.	5.0 vol.% 7.0 vol.%	~12% ~20%	[115]
Al_2O_3	Engine oil	Spherical ~28 nm diam.	5.0 vol.% 7.5 vol.%	~26% ~30%	[115]
Al	Engine oil	Spherical ~80 nm diam.	1.0 vol.% 3.0 vol.%	~20% ~37%	[186]
AlN	Mineral oil	Spherical ~50 nm diam.	0.05 vol.%	~8%	[187]
CuO	Mineral oil	Spherical ~100 nm diam.	2.5 vol.% 5.0 vol.% 7.5 vol.%	~12% ~23% ~43%	[84]
CuO_2	HE-200 oil (pumps)	Spherical ~36 nm diam.	0.052 vol.%	~44%	[12]

Filler	Type of oil	Nanoparticles morphology	Filler fraction	TC enhancement	Ref.
Diamond	Mineral oil	Spherical ~<10 nm diam.	1.0 vol.% 1.9 vol.%	~5% ~11%	[188]
Graphene	Mineral oil (50°C)	2D sheets ~500 by 500 nm ~8–10 atomic layer thick	0.01 wt.% 0.10 wt.%	~10% ~80%	[15]
Graphite	Heat transfer oil ¹ (LD320) at 30°C	Spherical ~10–30 nm diam.	0.34 vol.% 0.68 vol.% 1.36 vol %	~5% ~12% ~36%	[126]
h-BN	Mineral oil (50°C)	2D sheets ~500 by 500 nm ~5 atomic layer thick	0.01 wt.% 0.05 wt.% 0.10 wt.%	~9% ~10% ~80%	[15]
h-BN	Synthetic fluid	2D sheets ~500 by 500 nm ~5 atomic layer thick	0.10 wt.%	8%	[49]
MWCNT	Engine oil (15W-40)	Rods ~ Length: 0.3–10 µm Diameter: 10–50 nm	0.25 vol.% 0.5 vol.% 1.0 vol.%	~10% ~17% ~45%	[19]
MWCNT	Mineral oil	Rods ~ Length: 10–50 µm Diameter: 10–30 nm	0.5 vol.%	~8.5%	[76]
MWCNT	Synthetic PAO oil	Rods ~ Length: 50 µm Diameter: 25 nm	1.0 vol.%	160%	[170]
MWCNT	Synthetic engine oil	Rods ~ Length: µm range Diameter: 10–50 nm	1.0 vol.% 2.0 vol.%	~9% ~30%	[14]
MWCNT	Poly-α-olefin (PAO)	Rods ~ Length: 1–100 µm Diameter: 20–300 nm	1.0 vol.%	~175%	[19]
MWCNT	Poly-α-olefin (PAO6)	Rods ~ Length: µm range Diameter: ~25 nm	0.04 vol.% 0.25 vol.% 0.34 vol.%	~9% ~100% ~200%	[189]
CNTs	Poly-α-olefin (PAO)	Rods ~ Length: µm range Diameter: ~15 nm	0.10 vol.% 0.60 vol.% 1.0 vol.%	~35% ~96% ~161%	[176]
Exfoliated graphite	Poly-α-olefin (PAO)	2D sheets ~ µm range	0.10 vol.% 0.60 vol.% 1.00 vol.%	~18% ~56% ~130%	[176]

Notes: If not specified, measurements were conducted at room temperature.

¹With addition of dispersant (CH-5).

Table 2. Influence of oil-based nanofluids in thermal management.

Filler	Conventional fluid	Nanoparticles morphology	Filler fraction	TC Enhancement	Ref.
Al_2O_3	Water (RT ~25°C)	Spherical ~38 nm diam.	1.0 vol. %	~5%	[62]
	Water (50°C)		1.0 vol. %	~11%	
	Water (RT ~25°C)		4.0 vol. %	~12%	
	Water (50°C)		4.0 vol. %	~25%	
Al_2O_3	Water (RT ~21°C)	Spherical ~11 nm diam.	1.0 vol. %	~10%	[64]
	Water (50°C)		1.0 vol. %	~13%	
	Water (70°C)		1.0 vol. %	~15%	
Al_2O_3	Water (RT ~21°C)	Spherical ~47 nm diam.	1.0 vol. %	~3%	[64]
	Water (50°C)		1.0 vol. %	~6%	
	Water (50°C)		4.0 vol. %	~10%	
	Water (70°C)				
Al_2O_3	Water (RT ~21°C)	Spherical ~150 nm diam.	1.0 vol. %	~2%	[64]
	Water (50°C)		1.0 vol. %	~5%	
	Water (70°C)		4.0 vol. %	~8%	
Al_2O_3	Water	Spherical ~60 nm diam.	5.0 vol. %	~20%	[190]
Al_2O_3	Water (50°C)	Spherical ~131 nm diam.	1.0 vol. %	~11%	[191]
	Water (RT ~25°C)		4.0 vol. %	~10%	
	Water (50°C)		4.0 vol. %	~25%	
Al_2O_3	Water	Spherical ~27–56 nm diam.	1.6 vol. %	~10%	[192]
Au	Water	Spherical ~10–20 nm diam.	0.00026 vol. %	~8%	[11]
Ag	Water	Spherical ~60–80 nm diam.	0.001 vol. %	~5%	[11]
Cu	Water ¹ (+ CTAB)	Spherical ~60–100 nm diam.	1.0 vol. %	~48%	[193]
CuO	Water	Spherical ~36 nm diam.	1.0 vol. %	~12%	[12]
			5.0 vol. %	~60%	
CuO	Water	Spherical ~100 nm diam.	1.0 vol. %	~5%	[55]
			2.0 vol. %	~17%	
CuO	Water (RT ~25°C)	Spherical ~ 24 nm diam.	1.0 vol. %	~14%	[62]
	Water (50°C)		1.0 vol. %	~29%	
	Water (RT ~25°C)		4.0 vol. %	~15%	
	Water (50°C)		4.0 vol. %	~36%	
CuO	Water	Spherical ~ 100 nm diam.	2.5 vol. %	~24%	[84]
			5.0 vol. %	~55%	
			7.5 vol. %	~78%	
CuO	Water (RT ~25°C)	Spherical ~ 87 nm diam.	1.0 vol. %	~7%	[191]
	Water (50°C)		1.0 vol. %	~28%	
			4.0 vol. %	~15%	

Filler	Conventional fluid	Nanoparticles morphology	Filler fraction	TC Enhancement	Ref.
CuO	Water (50°C)		4.0 vol. %	~36%	[194]
	Water	Spherical ~ 25 nm diam.	0.10 vol. %	~7%	
			0.30 vol. %	~12%	
Graphene	Water	Sheets, 1 µm lateral	0.40 vol. %	~9%	[178]
Graphene & MWCNTs	Water	G sheets, 1 µm lateral; MWCNTs ~19 nm diam.	0.40 vol. %	~11%	[178]
Graphene nanoplatelets	Water	2D sheets, ~2 nm in thickness	0.01 wt. %	~28%	[179]
SiO ₂	Water	Spherical ~12 nm diam.	1.0 vol. %	~3 %	[76]
TiO ₂	Water	Spherical ~15 nm diam.	1.0 vol. %	~18%	[104]
			5.0 vol. %	~30%	
CNTs	Water (RT ~25°C)	Rods ~ Length: 35 µm	0.01 wt. %	~38%	[150]
	Water (60°C)	Diam.: 20 nm	0.10 wt. %	~126%	
	Water (60°C)		0.10 wt. %	~288%	
MWCNTs	Water	Rods ~ Length: 30 µm Diam.: 15 nm	1.0 vol. %	~7%	[171]

Notes: If not specified, measurements were conducted at room temperature.
¹With addition of cetrimonium bromide (CTAB).

Table 3. Influence of water-based nanofluids in thermal management.

Filler	Conventional fluid	Nanoparticles morphology	Filler fraction	TC enhancement	Ref.
Al ₂ O ₃	R141b refrigerant (20°C)	Spherical ~13 nm diam.	0.50 vol. %	~26%	[17]
			2.0 vol. %	~69%	
Al ₂ O ₃	Ethylene glycol	Spherical ~10 nm diam.	5.0 vol. %	~18 %	[83]
Al ₂ O ₃	Ethylene glycol	Spherical ~60 nm diam.	5.0 vol. %	~30%	[190]
Al ₂ O ₃	Ethylene glycol	Spherical ~28 nm diam.	5.0 vol. %	~25%	[115]
			8.0 vol. %	~40%	
AlN	Ethylene glycol	Spherical ~50 nm diam.	5.0 vol. %	~20%	[195]
			10.0 vol. %	~40%	
Au	Toluene	Spherical ~ 10–20 nm diam.	0.011 vol. %	~9%	[11]
Cu	Ethylene glycol ¹	Spherical ~ 10 nm diam.	~0.30 vol. %	~40%	[83]
Cu	Toluene	Spherical ~ 40–60 nm diam.	1.0 wt. %	~12%	[174]
			1.5 wt. %	~14%	
Cu	Kerosene (@25°C)	Spherical ~ 40–60 nm diam.	1.0 wt. %	10%	[174]

Filler	Conventional fluid	Nanoparticles morphology	Filler fraction	TC enhancement	Ref.
	Kerosene (@50°C)		1.0 wt.%	~15%	
CuO	Ethylene glycol	Spherical ~35 nm diam.	2.0 vol.%	~10%	[144]
			4.0 vol.%	~22%	
CuO	Ethylene glycol	Spherical ~23 nm diam.	~15.0 vol.%	~55%	[115]
Fe ₃ O ₄	Kerosene	Spherical ~15 nm diam.	0.50 vol.%	~15%	[119]
			1.0 vol.%	~34%	
Graphene	Ethylene glycol (20°C)	2D sheets, 500 nm by 600 nm	0.14 vol.%	6.5%	[141]
	Ethylene glycol (50°C)		0.14 vol.%	36%	
Graphene	Ethylene glycol (50°C)	2D sheets ~0.2–2.0 µm, thickness of 0.7–1.3 nm	2.0 vol.%	~40%	[180]
			5.0 vol.%	~86%	
h-BN	EcoDraw (50°C)	2D sheets ~500 by 500 nm ~5 atomic layer thick	0.01 wt.%	~25%	[49]
			0.10 wt.%	~30%	
h-BN	Montgomery (50°C)	2D sheets ~500 by 500 nm ~5 atomic layer thick	0.01 wt.%	~10%	[49]
			0.10 wt.%	~14%	
h-BN	Metkut (50°C)	2D sheets ~500 by 500 nm ~5 atomic layer thick	0.01 wt.%	~4%	[49]
			0.10 wt.%	~8%	
h-BN	Metkool (50°C)	2D sheets ~500 by 500 nm ~5 atomic layer thick	0.01 wt.%	~14%	[49]
			0.10 wt.%	~18%	
MWCNT	Ethylene glycol	Rods Length: 30 µm Diam.: 15 nm	0.05 vol.%	~7%	[196]
			1.0 vol.%	~13%	
MWCNT	Ethylene glycol	Rods Length: µm range Diam.: ~20–30 nm	0.50 vol.%	~8%	[14]
			1.0 vol.%	~13%	
SiC	Ethylene glycol	Whiskers Length ~18 µm Diam.: 1.5 µm	5.0 vol.%	~85%	[106]
SiO ₂	Ethylene glycol	Spherical ~23 nm diam.	1.0 vol.%	~4%	[40]
TiO ₂	Ethylene glycol/water (20/80 %)	Spherical ~21 nm diam.	4.0 vol.%	~15%	[197]

Notes: If not specified, measurements were conducted at room temperature.
¹With addition of <1 vol.% of thioglycolic acid.

Table 4. Influence of diverse nanofluids in thermal management.

4.2. Tribological performance

Tribology is a science and technology that describes the interaction between surfaces and their relative movement, practices and materials associated, including friction, lubrication, and wear. Friction and wear are two major causes of energy and material losses in mechanical processes. Friction plays a crucial role in diverse processes such as drilling, cutting, working pair components and mechanisms, among others; a measurement for this property, which is

becoming more relevant in today's life, is the COF (μ). Wear is a critical issue as components are in constant friction; a key measurement of the anti-wear properties of the lubricants and metal-cutting fluids is the WSD. Lubricants can be used to minimize contact friction between components, resulting in considerable energy and tooling savings [198]. The use of nanoparticles on lubricant nanofluids applications have the advantage of not to be temperature sensible and that tribo-chemical reactions are limited, compared to conventional additives [71, 199–201]. A great advantage is that in cooling applications, there could be higher energy savings and less pollution emissions. Moreover, it is very important to mention that some of these used nanoparticles are environmental friendly.

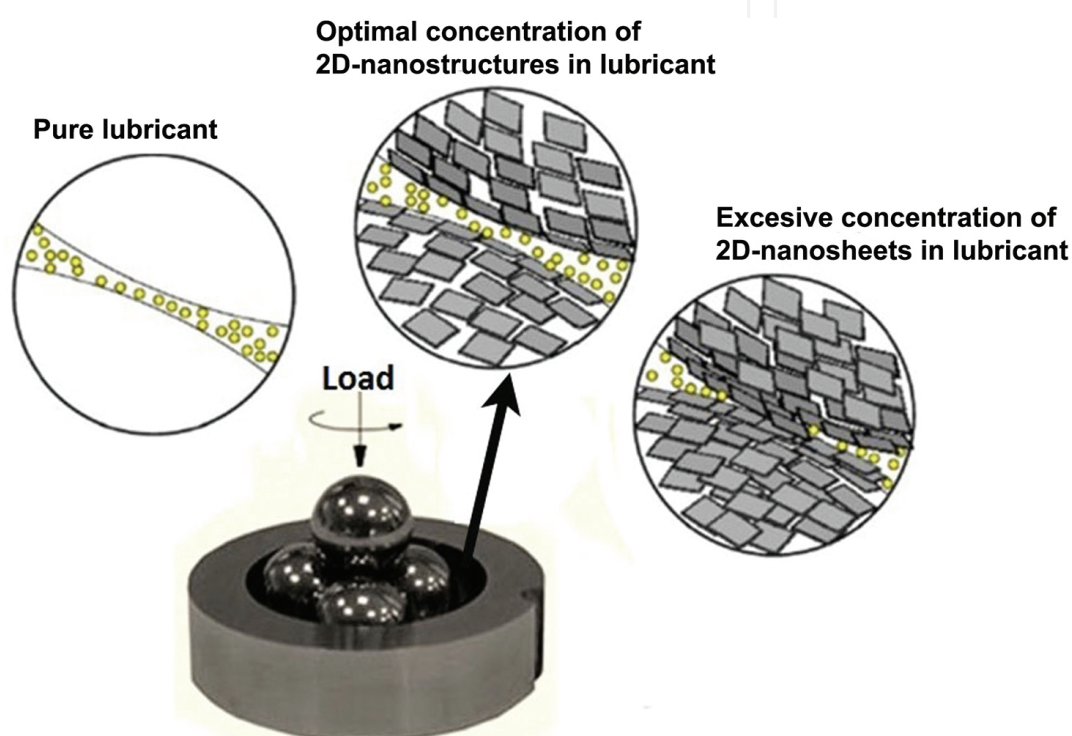


Figure 7. Schematic diagram of the tribological mechanism of nanosheets as lubricant additives.

The addition of nanoparticles (or nanoadditives) has been shown excellent enhancements in tribological properties in numerous fluids. Moreover, diverse mechanisms by which dispersed nanoparticles in lubricants result in lower friction and wear have been shown in the literature. These mechanisms include (i) reacting with the surfaces creating a transferred solid lubricant film from nanoparticles under the contact pressure [202, 203], (ii) rolling of nanoparticles in the contact zone, where the nanoparticles serve as a third body, which decrease the contact between the asperities of the two mating surfaces [204], (iii) reducing asperity contact by filling the valleys of contacting surfaces [71, 205, 206], (iv) shearing of trapped nanoparticles at the interface without the formation of an adhered film [207], and (v) tribosinterization of nanoparticles can occur on the wear surfaces forming a film which also prevent the direct contact of rubbing surfaces and reduce greatly the frictional force between the contacting surfaces [71, 208, 209]. As observed by Zhang et al. [204], a particular effect occurs when excessive concen-

tration of nanostructures is added to nanofluids. A threshold is reached and even though with higher filler fraction there is an improvement in tribological properties, there is an optimal filler fraction where wear is minimized, as it is explained by the tribological mechanism depicted in **Figure 7**. During tribological evaluation (four-ball tribotesting), components are in sliding contact, nanosheets can form a protective layer on the surface of each steel ball at lower concentrations, which introduces the enhanced anti-wear performance. However, as the nanosheets loading exceed a critical value, the fluid film will become discontinuous, degrading the anti-wear properties, finally leading to a dry friction.

Eswaraiah et al. [210] synthesized ultrafine graphene thru solar radiation exfoliation techniques (sheets ~ 300 nm by <2 nm thick). Nanofluids from these material and motor oil showed a decrease in COF of 80%, compared to base oil. This increase was attributed to the graphene tribological mechanism, which acted as nano-bearing within the oil, as well as for its excellent mechanical properties. It was explained by Hernández-Battez et al. [71] that nanoparticles could react with the surfaces, forming antifriction compounds and deposit on the wear surfaces by tribosinterization [71]. Moreover, Yu et al. [211] reported improved lubricating properties by adding 0.2 wt.% Cu nanoparticles to lubricant oil; in their study, Cu formed a soft film by friction-shearing and high pressure, reducing the COF up to 20%. As described by Peng et al. [212] during the friction process, a lubricating film of the nanoparticles is formed between the rubbed faces. The nanoparticles in the film not only bear the load but also separate the rubbing faces, dominating the reduction in the wear and friction.

Recently, Hu et al. [213] investigated the effects of MoS_2 nanosheets (30–70 nm in thickness) dispersed in LP. Average COF for 0.5 wt.% filler fraction of MoS_2/LP was reduced $\sim 60\%$, as well as WSD, which was reduced $\sim 8\%$, compared to pure LP. The anti-wear properties of the base fluid with MoS_2 nanosheets were improved remarkably by increasing the MoS_2 concentration up to 0.5 wt.%. According to Hu et al., due to the dimension and surface effect, it is ascribed that MoS_2 could enter into the gap of the friction pair, functioning as lubricator. Wu et al. [214] studied the effects of 2D nanosheets of MoS_2 with addition of 1.0 wt.% of span-80 (sorbitant monooleate) as a surfactant in LP. Results were also compared with MoS_2 microparticles (3–5 μm in diameter). It was shown that COF was reduced by $\sim 18\%$ at 1.5 wt.% MoS_2/LP ; furthermore, the COF of nanosheets were lower and more stable than that of microparticles due to the surface area effect [215]. As explained by Wu et al., the lubrication mechanism of layered 2D-nanosheets of MoS_2 was associated with the shearing of the weak Van der Waals bonds between molecular layers. When MoS_2 is used as an additive in base oils, besides molecules of base oils, MoS_2 powder is also adsorbed on the surface of substrates. Then the adsorbed MoS_2 is burnished and forms stable films, which can endure high loads and improve tribological performances of the base oil. Therefore, with addition of MoS_2 particles, the COF of base oil is reduced significantly. Similarly, Kao et al. [216] used TiO_2 nanoparticles as additives in paraffin oil to reduce the friction between cast iron components. Tribological studies revealed an enhancement of $\sim 24\%$ in COF at 60°C ; it was concluded that spherical nanoparticles provide good rolling to reduce friction between two parallel specimens, as nanoparticles could fill rough cracks in a metal wall surface to reduce the COF.

For the protection of mechanical components, from friction and wear in aerospace, automotive, military, and various industrial applications, an efficient lubricant is demanded; graphene is a widely known material for this purpose. More recently, BN has attracted attention, since it has similar properties as graphene. Among diverse applications, BN could improve lubricity properties of composites under friction or wear applications as well. Zhang et al. [217] and Saito et al. [218], for instance, have observed a decrease in COF with increasing temperature in composites containing BN and have attributed this to the lubricating nature of BN. Silver (Ag) is also used due to its relatively larger coefficient of diffusion and its nature to form low shearing stress junctions at sliding interfaces, resulting in good lubrication. However, h-BN high thermal stability, good chemical inertness, and high thermal conductivity, makes it suitable candidate to be a “clean” lubricant [217]. There are studies available in the literature on the coatings prepared by addition of h-BN. Leon et al. reported that Ni-P-hBN autocatalytic composite coating with 35 vol.% hBN sliding against steel ball at room temperature had a COF of ~ 0.2 [219], while steel on steel COF is ~ 0.8 . Avril et al. reported that laser melting hBN/ α -Fe(Cr) coating showed lower COF and better wear resistance than untreated steels under dry sliding within a temperature range of 25–500°C [220]. Spikes [221] stated that the most promising 2D sheet structures are carbon-based graphitic materials and the inorganic fullerenes. These showed low friction in boundary lubrication conditions in laboratory tests. Hence, for metal-mechanic and oil industry which deals with drilling, cutting, or other friction characteristics with working tools, this research will be suitable. **Table 5** shows the influence of 2D nanoparticles on tribological applications with COF and wear performance.

Filler	Type of Oil	Nanoparticles morphology	Filler fraction	COF decrease	Wear decrease	Ref.
CuO	Poly- α -olefin oil	Spherical ~ 30 – 50 nm diam.	2.0 wt. %	$\sim 54\%$	–	[71]
CuO	Poly- α -olefin (25°C)	Spherical ~ 20 nm diam.	0.20 wt. %	$\sim 5\%$	$\sim 13\%$	[211]
	Poly- α -olefin (80°C)			$\sim 10\%$	$\sim 21\%$	
	Poly- α -olefin (140°C)			$\sim 20\%$	$\sim 23\%$	
CuO	API-SF engine oil	Spherical ~ 5 nm diam.	~ 0.10 wt. %	$\sim 20\%$	$\sim 17\%$	[222]
CuO	SAE30 oil	Spherical ~ 5 nm diam.	~ 0.10 wt. %	$\sim 6\%$	$\sim 79\%$	[222]
Diamond	API-SF engine oil	Spherical ~ 10 nm diam.	< 0.10 wt. %	$\sim 4\%$	$\sim 43\%$	[222]
Graphene	Engine oil	Sheets ~ 300 nm, < 2 nm thick	0.025 wt. %	$\sim 80\%$	$\sim 33\%$	[210]
Graphene	Poly- α -olefin oil ¹	Sheets $\sim \mu\text{m}$ size	0.02 wt. %	$\sim 17\%$	$\sim 9\%$	[204]
			0.06 wt. %	$\sim 13\%$	$\sim 14\%$	
			1.00 wt. %	$\sim 12\%$	$\sim 12\%$	
MoS ₂	Graphene solid lubricant	Flakes (10–20 nm)	7–10 wt. %	$\sim 23\%$	$\sim 56\%$	[223]
Graphene	Ionic liquid (IL)	Sheets (monolayer 3.819 nm)	23 wt. %	$\sim 56\%$	$\sim 94\%$	[224]
MoS ₂	PAO	Nano sheets (5–10 nm thick)	5.0 wt. %	~ 30 – 40%	$\sim 75\%$	[225]
h-BN	CIMFLO 20 oil ²	Spherical ~ 70 nm diam.	1.0 wt. %	–	$\sim 55\%$	[205]
MoS ₂	CIMFLO 20 oil ²	Spherical ~ 70 – 100 nm diam.	4.0 wt. %	$\sim 10\%^2$	$\sim 65\%$	[205]

Filler	Type of Oil	Nanoparticles morphology	Filler fraction	COF decrease	Wear decrease	Ref.
TiO ₂	API-SF engine oil	Spherical ~80 nm diam.	~0.10 wt. %	~15%	~40%	[222]
WS ₂	CIMFLO 20 oil ³	Spherical ~50 nm diam.	4.0 wt. %	–	~66%	[205]

Notes: If not specified, measurements were conducted at room temperature.

¹Oleic acid was added ~5 vol. %.

²On steel/440C systems.

³On titanium/440C pairs.

Table 5. Influence of nanofluids (oil-based) in tribological applications.

5. Two-dimensional nanostructures

Initial studies on 1-D nanostructures got immediate attention soon after the landmark paper by Iijima [4] on CNTs in 1991 and various types of organic-inorganic 1-D nanostructures were realized thereafter [226]. More recent advances in layered materials enable large-scale synthesis of various two-dimensional (2D) materials [5, 15, 108, 210, 227, 228], where atoms are arranged in flat layers, which can be stacked on top of each other. One of the most common naturally layered materials is graphene, which has been widely studied for its superb properties and applications in diverse fields. 2D materials can be good choices as nanofillers in heat transfer fluids, as they have high surface area available for heat transfer.

A common production route of these layered nanostructures is exfoliation, where material individual layers are separate out from each other, either chemically or mechanically (i.e., abrasion) [15, 49, 108, 229–231]. It is important to mention that even though exfoliation can be achieved mechanically on a small scale [229, 230], liquid phase methods are required for diverse applications such as nanoelectronics, micro-electromechanical systems (MEMS)/nanoelectromechanical systems (NEMS), chemical and pressure sensors, etc. [231]. Another possible route to obtain these 2D structures is by direct chemical growth of individual layers (i.e., graphene sheets) through chemical vapor deposition (CVD) technique on the surface of a metals catalyst (i.e., copper, silica) by heating at high temperatures (~600–1200°C) and passing a carbon-containing gas such as methane over the catalyst [227]. A breakthrough research by Coleman et al. [108] showed that they were able to synthesize diverse 2D materials (MoS₂, WS₂, BN, Bi₂Te₃, MoSe₂, MoTe₂, NiTe₂, etc.) by wet exfoliation technique. Exfoliation of 2D insulators such as Bi₂Te₃, Bi₂Se₃, and h-BN would reduce its residual bulk conductance, highlighting surface effects. Another important aspect is that changes in electronic properties, as the number of layers is reduced as expected [108, 232]. This class of materials represents a diverse and largely unexploited source of 2D systems with interesting physic-mechanical and electrical properties, with high specific surface areas that is important for sensing, catalysis, and energy storage applications [108]. Hence, like graphene [5, 233], layered materials must be exfoliated to achieve their full potential.

6. Hexagonal boron nitride (h-BN)

In our research, main focus is on a novel 2D material, hexagonal boron nitride (h-BN), which is a ceramic material that exhibits versatile properties such as outstanding mechanical stability, remarkable chemical inertness, anti-wear promotion, high electrical resistivity, and superb thermal conductivity [5, 46, 234–239]. On the other hand, h-BN is an effective solid lubricant, it is suitable for diverse applications such as metal-working processes where lubrication at high-temperatures is required and is widely used in high-temperature wear-sealing materials of aerospace engines [155, 239]. Boron and nitrogen atoms behave similarly to carbon when bonded with each other to form boron nitride, exhibiting many similar structures as carbon only with alternating B and N atoms instead of C atoms (see **Figure 8**). Because of this, there are many forms of boron nitride (BN) that coincide with carbon structures and have a variety of properties and functions. h-BN (so-called “white graphite” due to its structural similarity to graphite) is a common form of BN that has a similar configuration to graphite which has been recently studied [15, 49, 108, 133]. Like graphite, this honeycomb layered material has hexagonal ring layers separated by 3.33 Å, in which every boron atom is connected to three nitrogen atoms by strong covalent bonds and vice versa; the B-N distance is 1.44 Å. Between the layers, every boron interacts with a nitrogen atom through a Van der Waals force [237, 240]. Therefore, the strong B-N bond makes an h-BN atomic layer a mechanically strong material, quite analogous to graphene, and individual BN layers could be isolated from bulk h-BN crystals [15, 108, 229]. As an insulating material with very high thermal conductivity [241], h-BN surpasses other nanofillers and is an attractive material for high thermal transport and electrically insulating composites [15, 133, 236, 242]. Nevertheless, theoretical studies indicate that high thermal conductivities can only be achieved from the (002) planes (up to hundreds to thousands of W/m K) [50, 243]; through a synthesis process of wet exfoliation, h-BN can give maximum exposure to these (002) lattice planes. Meantime, some thermal management systems need electrically conducting fillers for static electric charge dissipation. Graphene-based systems are good for these applications where they can do both thermal and electrical management. This shows how h-BN will be specially applicable and useful in thermal management applications, where electrical insulation is also required. It is also important to mention that BN is environmentally and skin friendly; proof of this is that BN is widely used as the main ingredient for cosmetics. According to the Cosmetic Ingredient Review (CIR) report from 2012, BN is used in 483 cosmetic formulations. Products containing BN are reported to be used on baby skin (in a lotion, oil, powder, or cream), eye area, or mucous membranes. BN is reported to be used at up to 25% in eye product formulations, at 2% in lipstick formulations, up to 16% in powders, and at up to 0.9% in fragrance preparations [244]. Hence, since little research have been conducted on 2D nanostructures, and particularly on boron nitride, exfoliated h-BN, having a few layers in thickness has a remarkable opportunity to overcome the material of the future in the thermal management field for diverse applications, including electrical/electronic, since its nature allows it to be a thermal conductor but an electrical insulator.

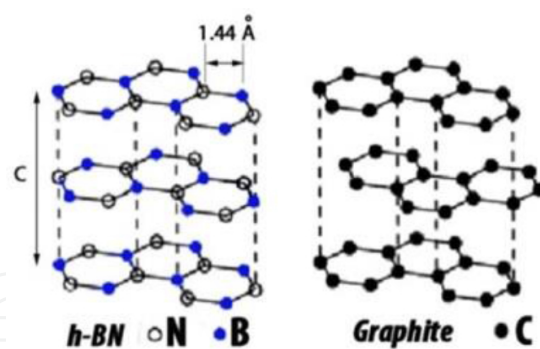


Figure 8. Scheme of h-BN and graphite structure.

7. Summary

The present work offers a general overview of the recent research and development on preparation and characterization of nanofluids for thermal management and tribological applications, with emphasis on experimental data, variables and features, as well as proposed mechanisms responsible for nanofluids improvement performance. Nowadays, many technologies search for the highest efficiency, mainly and more than ever before, on the cooling and anti-wear challenges within machines, devices and components. Several efforts have been made trying to homogeneously disperse nanostructures (oxides, metals, ceramics, CNTs, 2D-nanosheets and others) within conventional fluids to improve their properties, such as thermal transport, viscosity, lubrication, electrical behavior, among others. Nanofillers size has positive effect on conventional fluids performance, that is compared to larger dispersed solid particles making flow through small channels much more easier, also since diverse parameters are critical for devices performance, such as morphology and stability of dispersed nanostructures within conventional fluids, fluids composition, viscosity, fast sedimentation, channels clogging, wear or erosion, among others, which are often very serious for systems consisting of small channels. Furthermore, properties improvement is also dependent of various factors, such as filler fraction, temperature, chemical, and interfacial properties on the nanostructure-fluid interfaces. Some nanofluids are currently expensive, partly due to the difficulty in manufacturing. Hence, mass production of nanostructures could further decrease the cost, also low filler fraction is necessary to make nanofluids more affordable before they will see widespread applications.

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