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Thermal Conductivity of Al_2O_3/Water-Based Nanofluids: Revisiting the Influences of pH and Surfactant

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Abstract**—**The present work focuses on the preparation and the stabilization of Al_2O_3-water based nanofluids. Though they have been widely considered in the past, to the best of our knowledge, there is no clear consensus about a proper way to prepare and stabilize them by the appropriate surfactant. In this paper, a careful experimental investigation is performed to quantify the combined influence of pH and the surfactant on the stability of Al_2O_3-water based nanofluids. Two volume concentrations of nanoparticles and three nanoparticle sizes have been considered. The good preparation and stability of these nanofluids are evaluated through thermal conductivity measurements. The results show that the optimum value for the thermal conductivity is obtained mainly by controlling the pH of the mixture and surfactants are not necessary to stabilize the solution.

Keywords**—**Nanofluid, thermal conductivity, pH, transient hot wire, surfactant, Al_2O_3, stability, dispersion, preparation.

I. INTRODUCTION

NANOFLUIDS are a new class of fluids with enhanced thermophysical properties, which can be applied in many thermal devices for better performances. A complete, unique and well established definition unfortunately does not exist to date. This can be explained by the fact that the field is very recent and some concepts are not yet entirely understood. However, several definitions can be found in the literature, almost all of them are inspired by the first definition announced by Choi and Eastman [1]. They defined "nanofluids" as innovative heat transfer fluids, which can be designed by suspending nanoparticles into conventional fluids. Thirteen years later, the authors have revisited this definition in a book entitled *"Nanofluids, Science and Technology"* [2]. This new definition emphasizes the preparation step of nanofluids and the importance of the nanoparticle size. It also clearly emerges dispersion and stabilization as key elements for the good preparation of nanofluids. This definition can be found in [2] and summarized as: "Nanofluids are engineered by suspending nanoparticles with average sizes below 100 nm in traditional heat transfer fluids such as water, oil, and ethylene glycol. A very small amount of guest nanoparticles, when dispersed uniformly and suspended stably in host fluids, can provide dramatic improvements in the thermal properties of host fluids".

The Maxwell's theory [3] revealed that an improvement of the thermal conductivity may be obtained by scattering millimeter or micrometer-sized solid particles into a base fluid. However, one major disadvantage related to the use of such large particles is their rapid settling, which may result into a complete separation of the two phases and so causes a decrease of the resulting thermal conductivity. As opposed to milli- or micro-sized suspensions, nanofluids achieved by introducing metallic, non-metallic or polymeric nanoparticles are more stable. Furthermore, nanoparticles benefit from a 10^3 times larger surface/volume ratio than that of microparticles and exhibit then much higher thermal conductivity.

There are numerous researches on the superior heat transfer properties of nanofluids especially on the thermal conductivity. Choi and Eastman [1], Eastman et al. [4], Liu et al. [5], Hwang et al. [6], Yu et al. [7] and Mintsa et al. [8] observed an important improvement of the nanofluids' thermal conductivity compared to conventional coolants. Nevertheless, because of the difficulties in preparing comparable nanofluids and adjusting all the preparation parameters and the experimental conditions, the literature results are often contradictory. For example, Buongiorno et al. [9] performed a benchmark study on the thermal conductivity of nanofluids and did not observe anomalously high thermal conductivity enhancement. There is a wide range of techniques to measure the thermal conductivity of liquids, such as the cylindrical cell method, temperature oscillation method, steady-state parallel-plate method, 3ω method, thermal constants analyzer method, thermal comparator method, and hot disk method or transient hot-wire (THW). Some researchers argued that the non-observation of the anomalous enhancement in some data is due to the inaccuracies of some thermal measurement methods [10], [11]. Indeed, some measurement techniques, initially designed for solid, are not suitable for the measurement of the liquid conductivity being very affected by natural convection effects. KD2Pro Thermal Property Analyzer manufactured by Decagon Devices, Inc. may be cited as the best example. This instrument is mistakenly recurrently presented as a measurement technique based on the THW method while it is not as reliable. In the benchmark performed by Buongiorno et al. [9], the thermal conductivity tests were based, largely, on this non accurate device, which may render highly questionable the conclusions drawn in this paper.

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The present study is aimed to demonstrate experimentally that, by using appropriate measurement techniques and by optimizing the preparation conditions, it is possible to observe an increase in the thermal conductivity of nanofluids, much higher than the one predicted by the classical Maxwell's theory [3].

Alumina/water based nanofluid is probably the most studied nanofluids. Such suspensions are mainly created using two-step methods by dispersing Al_2O_3 nanoparticles into base liquids. The stabilization steps involve using the appropriate surfactant, controlling the pH of the solution and dispersing the nanoparticles by mechanical or ultrasound techniques. Several experimental studies [10]-[13] focused on the Al_2O_3/water nanofluids and revealed that their properties depend on a large number of parameters such as the size of nanoparticle, their volume fraction, the type and the concentration of the surfactant and the pH of the mixture. Effectively, because of the high surface energy of nanoparticles, it is easy for nanoparticles to coalesce and difficult to disperse them in water. Consequently, controlling the agglomeration of the nanoparticles has become a primary issue.

Huang et al. [14] investigated the dispersion behavior of Al_2O_3/water based nanofluids. The authors measured the absorbency and zeta potential of the suspensions under different pH values. The results indicated that the stability of nanofluids was highly dependent on the pH values. Xie et al. [15] compared the thermal conductivity of various suspensions containing Al_2O_3 nanoparticles. The pH of the mixture was adjusted at three different values: 4, 7 and 11.5. The highest enhancement observed for 60.4 nm sized particle at a concentration level comprised between 1.8 and 5 vol.% was obtained for a pH equal to 4. Khairul et al. [16] studied the effects of surfactant on the stability and thermo-physical properties of metal oxide nanofluids. They found that the variation of weight concentrations of sodium dodecylbenzene sulfonate (SDBS) has an effect on pH, zeta potential, particle size distribution, viscosity and thermal conductivity of Al_2O_3/ DI-water. Dehkordi et al. [17] measured the dynamic viscosity and thermal conductivity of alumina/water nanofluids with the addition of SDBS. They observed that low concentrations of SDBS have a negligible effect on both the thermal conductivity and viscosity of the suspension, while at higher concentrations (>1 wt.%) SDBS leads to a reduction of the thermal conductivity and an augmentation of the viscosity which undesirably affects the application of SDBS for nanofluids.

Other studies dealing with the effects of surfactant and pH on the properties of alumina/water nanofluids exist, except that these studies focused much more on the stability indicators (zeta potential, absorbency, particle size…) [18]-[20]. Studies on the optimization of the thermal conductivity based on two methods of pH control and surfactant addition exist but these works are usually done at low concentrations of nanoparticles or made based on inappropriate measurement techniques [16], [21]-[25].

The present study aims to investigate the effect of pH control and SDBS dispersant on the thermal conductivity of Al_2O_3/water nanofluids. The goal is to identify the optimal preparation conditions for these two parameters through direct conductivity measurements at particle concentration levels that are found in applications covered by nanofluids (between 0.2 and 2% vol). Once these parameters are selected, the effects of the particle size and concentration at the optimal conditions of preparation are examined in details.

II. EXPERIMENTAL METHODS

A. Measurement Technique for the Thermal Conductivity

The thermal conductivity of nanofluids is measured using the THW-L1 Liquid Thermal Conductivity System from Thermtest Thermophysical Instruments (Fig. 1). It measures the thermal conductivity, denoted k, based on the THW method. Coupled with a system controlling the temperature (heat exchanger + thermostat bath circulator), this device allows a complete characterization of the nanofluid thermal conductivity within the ranges -40 °C to 200 °C and $0.01 \leq k \leq 2$ W/(m.K). The THW-L1 allows a direct, accurate and fast measure of the thermal conductivity and diffusivity. The most important advantage of this method for its application to fluids is its capacity to experimentally eliminate the error due to natural convection. The principle of the hot-wire method is based on an ideal and constant heat generation source, an infinitely long and thin continuous line, dissipating the heat into an infinite test medium. A constant current is supplied to the wire (platinum) to generate the temperature rise. The wire serves as both the heat source and the temperature sensor [26]. Heating the wire by Joule effect causes the variation of its resistance, thus its temperature is measured as a function of time using a Wheatstone bridge and a data acquisition system. Finally, the thermal conductivity value is determined from the heating power and the slope of temperature change in a logarithmic time scale. Higher the thermal conductivity of the surrounding liquid is, lower will be the temperature rise of the wire [27]. The THW-L1 sensor has two key components: A thin platinum wire for heating the sample and recording raw data for the determination of the thermal conductivity and a PT100 Platinum resistance thermometer for independently measuring the temperature of the sample. The THW sensor (including the sample cell) is made of stainless steel. The platinum wire is 0.1 mm in diameter and 35 mm in length. A platinum wire is chosen owing to its capable resistance–temperature relationship over a wide temperature range. Nanofluids containing metal particles are electrically conductive. Teflon spray is then used for the coating of the platinum wire to act as an electric insulation.

The main experimental cell (sample cell) is in fact a part of the Wheatstone bridge circuit for which the resistance of the wire has to be measured. In the bridge, two of the four resistors are the fixed resistors. The third resistance is variable which allows balancing the circuit. The required sample volume is 50 ml.

The THW sensor is positioned at the center of the nanofluid sample cell and is placed inside the heat exchanger connected to the thermostat bath circulator to ensure constant-temperature test. Water is used as the heating fluid in the bath.

Fig. 1 THW-L1 Liquid Thermal Conductivity System from Thermtest Thermophysical Instruments

B. Preparation of Alumina-Water Nanofluids

The preparation of nanofluids is the first step towards the characterization of their properties. There are two primary methods to obtain nanofluids: The single-step method (direct evaporation) and the two-step preparation method [12]. In this study, the mixtures are prepared based on the two-step method, which consists in the dispersion of nanoparticles in powder form into the base liquid. Stability is a big issue that is inherently related to this operation as the powders easily aggregate due to strong van der Walls forces between nanoparticles. In spite of such disadvantages, this process is still popular as the most economic process for nanofluid production at a large scale [28]. In addition, particles in dispersion may adhere together and form aggregates of increasing size which may settle out due to gravity. Stability means that the particles do not aggregate at a significant rate. At this stage of the preparation, it is necessary to act in order to improve the dispersion and stability of suspension by chemical and mechanical ways. The most common methods of dispersion are: Addition of acid or base to modify the pH value of the suspension and consequently to control surface potential; addition of surfactants to prevent particles coming close to each other and the use of ultrasonic agitation.

The alumina nanoparticles used in our experimental protocol were directly purchased from US Research Nanomaterials, Inc, Houston, USA. The major part of our tests were performed with Al_2O_3 nanoparticles (80% alpha: 20% gamma, Purity: 99.9%, Size: 50 nm). In order to examine the effect of particle size on the thermal conductivity of suspensions, other alumina particles were used, their sizes varying from 50 nm to 1 µm. The anionic surfactant SDBS in technical grade, from Sigma-Aldrich Canada Co. (Oakville, Canada), was used for stabilizing the suspension. The pH was controlled using hydrochloric acid (HCl) and sodium hydroxide (NaOH) in analytical grade. The pH of the solution was measured with LabQuest 2 from Vernier (Beaverton, USA). Connected to the pH sensor and the temperature probe, this device offers the possibility to perform the simultaneous measurement of pH and temperature of the mixtures, which allows to obtain pH taking into account the correction due to the test temperature. Q700 Sonicator from Qsonica Sonicators is the ultra-sonicator used for the dispersal of particles in our experiences. This device is capable of delivering 700 watts, with a 20 kHz frequency. It delivers energy in forms of sound waves which can break the clusters. It can work in a continuous way for 72 hours or in an interrupted way. During the preparation of samples, it can be programmed to work in an interrupted way to avoid the overheating of samples. In addition, the preparation is plunged into a jacketed glass beaker, which is connected to a thermostat bath circulator.

C. Experimental Procedure

The first step in our experimental procedure is the weighing of the nanoparticles. Small and precise masses are measured with an analytical balance ("lab balance" 0.01 mg). This allows to obtain nanofluids with an ultra-precise concentration. In order to properly disperse the nanopowder into the water, nanoparticles must be homogenized in the medium. Since the purity of the nanofluid is important, particular attention has been made to avoid impurity. Particles are mixed directly with water with no additive. A first homogenization is made using a magnetic stirrer. During this mechanical agitation, depending on the test to be performed, pH adjustments and the addition of surfactant may be carried out. The most effective method of breaking and evenly dispersing the nanopowder in a fluid is through application of ultrasonic vibration. Using this methodology, the water/ alumina nanofluid was created and ultrasonic vibration was applied for generally 12 hours with 50% amplitude in an interrupted way (5s ON/2s OFF) for 500 ml of nanofluid. This initial solution of 500 ml was each time divided into samples of 50 ml, which were sonicated between 10 min and 30 min for each experience. This initial solution of 500 ml was each time divided into samples of 50 ml which were sonicated between 10 min and 30 min for each test.

The next step is to calibrate the THW using a reference solution (Water Deionized Ultrafiltered Water DIUF). The reference exhibits a thermal conductivity equal to 0.6052 W/(m.K) at 20 °C. For that, we begin by turning on the temperature bath with a fixed temperature of 20 °C and by putting the reference in the THW cell. Then, we change the bath’s temperature to 25 °C which is the fixed temperature of our experiences. The nanofluid was heated to the desired temperature after sonication. After taking the reading for each sample, the nanofluid was taken out and sonicated well before conducting the experiment for the next sample. During the experimentation, for well stabilized samples, we did not find any agglomeration for the nanofluid tested. For every sample, the glass beakers and the THW cell was well cleaned and dried with compressed air. The above procedure was repeated for different SDBS concentration, pH values, particle sizes and different volume concentrations of alumina nanoparticles.

III. RESULTS AND DISCUSSIONS

A. Effect of SDBS on the Thermal Conductivity at an Arbitrary pH Value

In the first experiment, the surfactant effect without adjusting the pH of the nanofluid is studied. In other words, the thermal conductivity *k* (W/ (m.K)) of the solution at different SDBS concentrations without fixing the pH is measured. This experiment is conducted using an initial solution of 500 ml of alumina/water nanofluid. Then, it is divided into several samples of 50 ml. The conditions of preparation are mentioned in Table I. The results of this experiment are shown in Fig 2.

TABLE I
CONDITIONS OF THE FIRST EXPERIENCE (VARIATION OF THERMAL CONDUCTIVITY AND PH WITH WEIGHT FRACTION OF SDBS)

Size of nanoparticles	50 nm
Volume fraction Al_2O_3	2 Vol.%
Weight fraction of SDBS	0 to 0.05 wt.%
Ultrasonication	12 h for 500 ml ***10*** min for each 50 ml
Temperature	25 °C

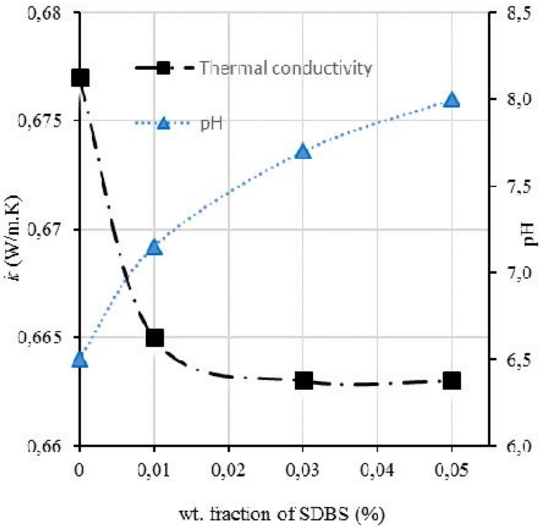

Fig. 2 Variation of the thermal conductivity and pH with weight fraction of SDBS

As seen in Fig. 2, the addition of SDBS modifies the pH value. Moreover, the conductivity is not improved with the adjusted concentration of SDBS and this is because the pH values are not in the optimal range. The maximum enhancement (compared to distilled water, *k* (water, 25 °C) =0.613 W/(m.K)) is attained here when the SDBS is not used (0 wt.%) and it is found to be 10.4% whereas, with the use of SDBS, one obtains an enhancement of around 8%.

The next step is then to identify the optimal range of SDBS concentration by improving the preparation conditions (sonication time). As in the first experience, the pH of the solutions is not adjusted and each sample has its own pH value depending on the quantity of added SDBS. The new preparation conditions as well as the results are presented in Table II and Fig. 3 respectively.

As seen in Fig. 3, the conductivity reaches its optimal value at 0.03 wt.% of SDBS with an enhancement of 13.2% compared to distilled water (base fluid). In fact, improving the nanofluid conductivity can be obtained by optimizing the surfactant percentage but it is not necessary that one get an optimal value as the pH is not fixed yet. Thus, combining both effects to determine the optimal percentage of surfactant for a fixed pH value is imperative. Therefore, in order to fix an optimal range of pH values, a study of the pH effect on the thermal conductivity was conducted.

TABLE II
CONDITIONS OF THE SECOND EXPERIENCE (VARIATION OF THERMAL CONDUCTIVITY WITH WEIGHT FRACTION OF SDBS WITHOUT FIXING THE PH VALUE)

Size of nanoparticles	50 nm
Volume fraction Al_2O_3	2 Vol.%
Weight fraction of SDBS	0 to 0.3 wt.%
Ultrasonication	12 h for 500 ml ***30*** min for each 50ml
Temperature	25 °C

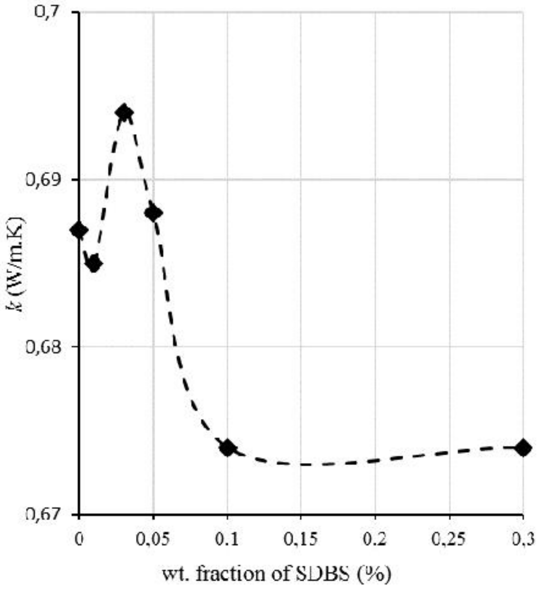

Fig. 3 Variation of the thermal conductivity with weight fraction of SDBS without fixing the pH value

B. Effect of pH on the Thermal Conductivity

In this series of tests, one aims to isolate the effect of pH on the thermal conductivity *k* (W/(m.K)). Alumina-water mixtures at the same volume fraction (2 Vol.%) are prepared without addition of surfactant. The pH of solutions is varied from 3.5 to 7.5. For pH values outside this range, visual examination of the stability shows a strong sedimentation which explains the uselessness of presenting them in the conductivity measurements. The conditions of this experiment as well as the results are presented in Table III and Fig. 4 respectively. This study shows that an increase of the conductivity of more than 15% can be observed when the pH of the solution is between 5.3 and 6.1 and without addition of surfactant, values which are not reached with the use of the SDBS at random pH values. Based on these results, a new study of the pH effect on the conductivity is made. The range of pH values from 5.3 to 6.1 is investigated to identify more precisely the optimal pH value (Fig. 5).

This study showed that the preparation of nanofluids is strongly dependent on the pH value. As it can be seen on Fig. 5, the adjustment of the pH causes the improvement of the thermal conductivity. An enhancement of 21% is observed at pH=5.7 (optimal pH). To generalize this result to other particle sizes, the effect of the pH on the thermal conductivity is studied for three different sizes, namely 50 nm, 135 nm and 200 nm. The experience is conducted without adding SDBS and the concentration of Al_2O_3 nanoparticles in water is fixed to 2 vol%. All conditions are presented in Table IV, and the test results are illustrated in Fig. 6 which shows the evolution of the relative improvement in the thermal conductivity of nanofluids compared to the base fluid ($R=k_{nf}/ k_{bf}$).

TABLE III
EXPERIMENTAL CONDITIONS (PH EFFECT)

Size of nanoparticles	50 nm
Volume fraction Al_2O_3	2 Vol.%
Weight fraction of SDBS	Without addition of surfactant
Ultrasonication	12 h for 500 ml **15** min for each 50ml
Temperature	25 °C

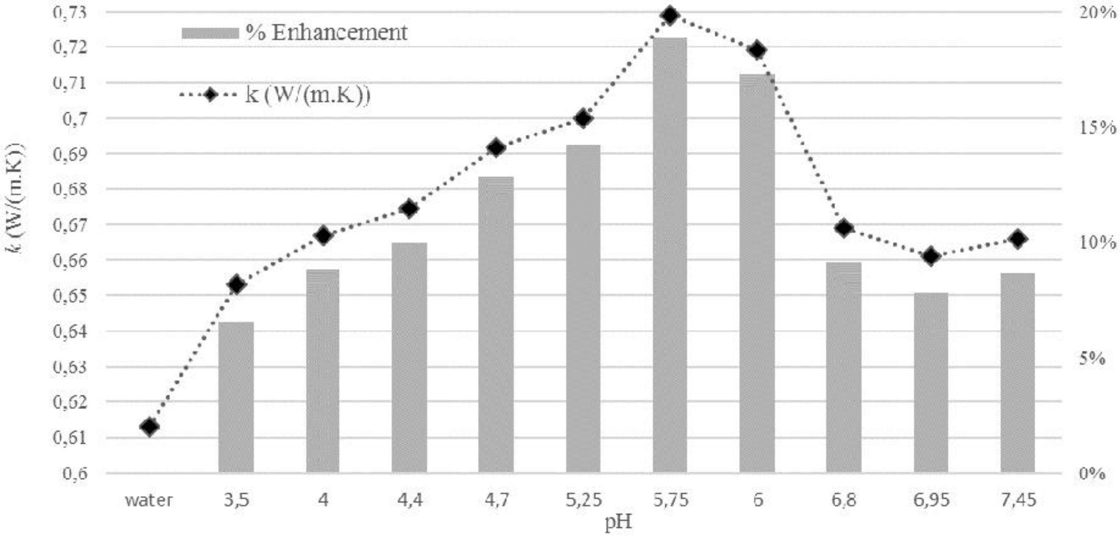

Fig. 4 Thermal conductivity as a function of pH with the enhancement percentage without adding SDBS

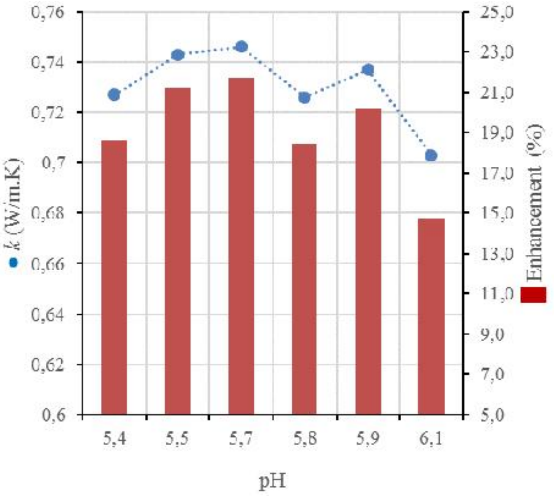

Fig. 5 Thermal conductivity as a function of pH (optimal range)

As seen in Fig. 6, the variation of the thermal conductivity with pH is not linear and an optimal zone between 5.4 and 5.8 may be identified for the three sizes. Thus, an approximation is made and the optimal pH value is fixed to 5.7 for the three sizes for the further experiences.

TABLE IV
EXPERIMENTAL CONDITIONS (PH EFFECT FOR DIFFERENT SIZES)

Size of nanoparticles (nm)	50, 135 and 200
Volume fraction Al_2O_3	2 Vol.%
Weight fraction of SDBS	0
Ultrasonication	12 h for 500 ml **25** min for each 50 ml
Temperature	25 °C

The maximum enhancements are 21.7%, 14.2% and 11.7% for 50 nm, 135 nm and 200 nm respectively. In the case of 200 nm particle size, the conductivity values know a degradation while measuring. This can be explained by the fast sedimentation caused by the large particle size compared to the two other sizes. Fig. 6 also shows the enhancement of the thermal conductivity with the size of particles. In fact, when the size becomes larger, the thermal conductivity becomes lower. This result is also proved in Section III *D*.

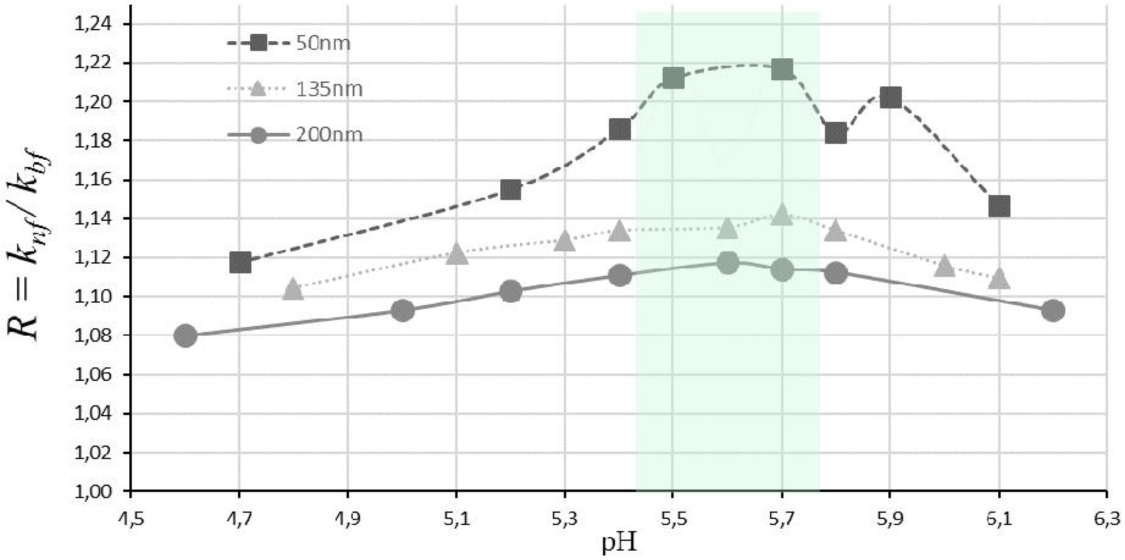

Fig. 6 Thermal conductivity as a function of pH for different nanoparticle sizes

C. *Effect of the SDBS Surfactant on the Thermal Conductivity at Adjusted Optimum pH*

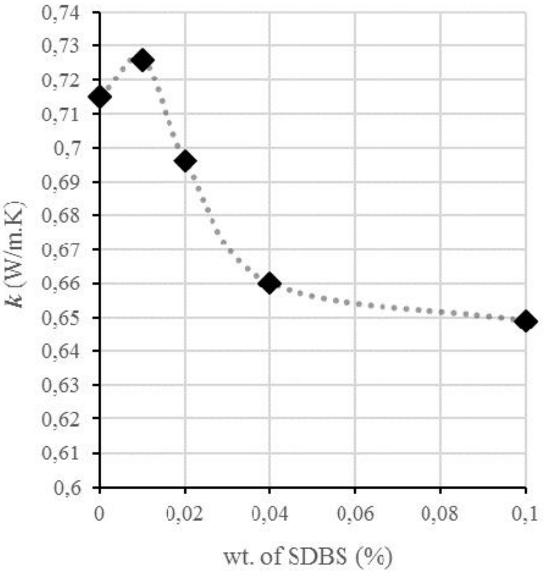

Fig. 7 Variation of the thermal conductivity with the weight fraction of SDBS at fixed optimum pH

TABLE V
Experimental Conditions (SDBS Effect at Adjusted Optimum pH)

Size of nanoparticles	50 nm
Volume fraction Al_2O_3	2 Vol.%
Weight fraction of SDBS	0 to 0.1 wt.%
pH	5.7
Ultrasonication	11 h for 500 ml **15** min for each 50ml
Temperature	25 °C

After fixing an optimal pH, a study of the SDBS effect at that optimal pH value is needed. In order to do that, various 50 ml samples from a 500 ml sonicated solution are prepared. After adding the suitable SDBS concentration for each sample, the pH value is readjusted to 5.7. The preparation conditions for this experience as well as the results are presented in Table V and Fig. 7 respectively.

Fig. 7 shows that the thermal conductivity values decrease rapidly in a remarkable way as soon as the SDBS concentration exceeds 0.02 wt.% and a peak is observed at 0.01 wt.%. Thus, we decided to explore better the range of values between 0 and 0.04 wt.%. To make sure that the range of concentrations from 0.04 wt.% SDBS is not suitable, a verification through the sedimentation method is made. This test allows us to study the stability of suspensions with a fixed SDBS concentrations and a variable pH. An example of these visual inspections is illustrated by Figs. 8 and 9 in which the SDBS concentration is fixed at 0.1 wt.% and pH at a random value for each sample. For this SDBS concentration (0.1 wt.%), it can be noticed that for any pH value a strong sedimentation occurs. In addition, the conductivity measurement at pH=5.7 gives a value clearly lower than that without SDBS: *k* (0.1 wt.% SDBS, pH=5.7)=0.649 W/(m.K) while *k* (0 wt.% SDBS, pH 5.7)=0.741 W/(m.K). The percentage of SDBS is downgraded by browsing the concentration range between 0.04 wt.% and 0.1 wt.%, which leads to a slight improvement in conductivity compared to 0.1% but still has strong signs of sedimentation and a conductivity value well below to that without surfactant: *k* (SDBS 0.04 wt.%, pH=5.7)=0.661 W/(m.K). These surfactant concentration levels are detrimental to the dispersion and the stability of the mixtures. Visual examinations of the agglomeration and sedimentation of these mixtures at these surfactant concentration levels substantially lead to the same conclusion than that relating to the SDBS concentration 0.1 wt.%. It is only by being at SDBS concentrations of 0.03 wt.% or less that the stability of the suspensions is improved. This finding is proved by the sedimentation method (see Figs. 10

and 11).

Fig. 8 Samples at different pH values from 4 to 7.5, at 0.1 wt.% SDBS

Fig. 9 Samples at 0.1 wt.% SDBS and different pH values, from left to right: pH=8 - 9.3 - 10 - 10.7 - 11.4 - 2 - 2.6 – 3

Fig. 10 Samples at 0.01 wt.% SDBS and different pH values, from left to right: pH=7.2 - 6.9 - 6.5 - 6.3 - 5.9 - 5.6 -5.3 – 5 - 4.8 - 4.5 - 4.2 - 4

Fig. 11 Samples at 0.015 wt.% SDBS and different pH values, from left to right: pH=6.4 - 6.6 - 7.1 - 6 - 5.8 - 5.6 - 5.4 - 5.2 - 4.9 - 4.5 - 3.9

As it can be noticed that the stability of mixtures with SDBS concentrations less than 0.03 wt.% improves when the value of the pH is around 5.7. Quantification of the effect of the surfactant concentration at this level (< 0.03 wt.%) at an optimum pH (5.7) on the thermal conductivity is then necessary. In order to achieve that, another experience is conducted and the time of sonication for each sample is increased for better stability. Measurements of the thermal conductivity are realized by fixing the pH to 5.7 and by varying finely the percentage of SDBS from 0 to 0.03% wt. The preparation conditions for this experience as well as the results are presented in Table VI and Fig. 12 respectively.

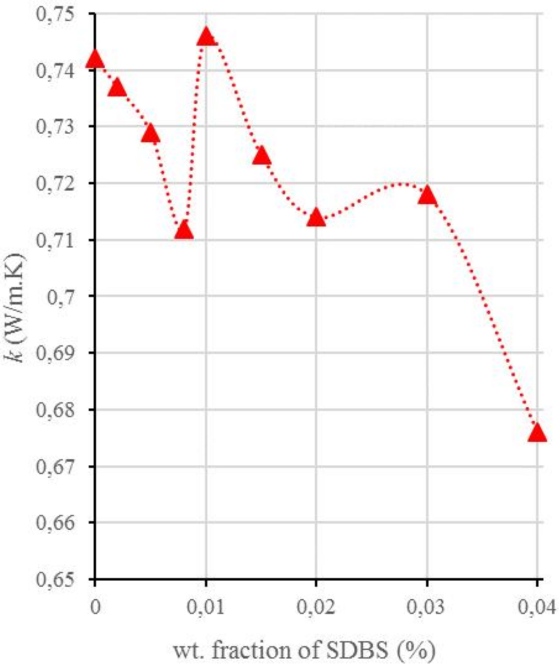

Fig. 12 Variation of the thermal conductivity with the weight fraction of SDBS at optimum pH

As seen in Fig. 12, the optimal percentage of SDBS should not exceed 0.03 wt.%. Besides, the addition of SDBS when the pH is optimized does not imperatively enhance the thermal conductivity as for some SDBS concentrations, lower conductivity values are observed compared to that of optimized pH without SDBS. In fact, the evolution of the conductivity as a function of the SDBS concentration is not linear and exhibits a peak at 0.01 wt.%. This value is noticed as the optimal one with an enhancement of 21.7% compared to pure water (base fluid).

TABLE VI
EXPERIMENTAL CONDITIONS (SDBS EFFECT – OPTIMUM RANGE)

Size of nanoparticles	50 nm
Volume fraction Al_2O_3	2 Vol.%
Weight fraction of SDBS	0 to 0.03 wt.%
pH	5.7
Ultrasonication	12 h for 500 ml **30** min for each 50ml
Temperature	25 °C

D. Effect of the Nanoparticle Size on the Thermal Conductivity

To study the effect of the nanoparticle size on the thermal conductivity, two experiments are conducted at two different concentrations i.e. 1 vol.% and 2 vol.%. These experiences are then compared to the Maxwell's model [3] for each concentration. The preparation conditions for this experience as well as the results are presented in Table VII and Fig. 13 respectively.

TABLE VII
EXPERIMENTAL CONDITIONS (SIZE EFFECT)

Size of nanoparticles (nm)	50 – 135 - 200 - 300 - 500 and 1000
Volume fraction Al_2O_3	1 and 2 Vol.%
Weight fraction of SDBS	0
pH	5.7
Ultrasonication	12h for 500ml **30** min for each 50ml
Temperature	25 °C

As it can be seen in Fig. 13, the thermal conductivity ratio decreases with the increase of the particle size for both concentrations of Al_2O_3. Comparing the experimental results with the Maxwell's model [3], one can see that when the size of the nanoparticles becomes small (below 300 nm), there is a strong improvement of the thermal conductivity values. However, the Maxwell model gives almost a constant improvement for different sizes. Thus, one can conclude that this classical model is not valid for nanoparticles.

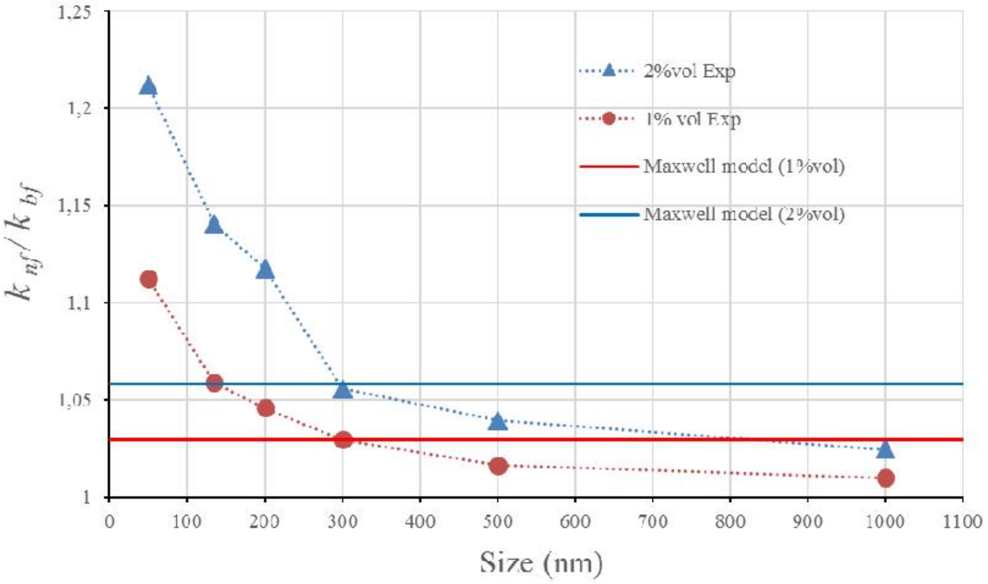

Fig. 13 Variation of the thermal conductivity ratio with the size of nanoparticles

Fig. 13 demonstrates that, by using the appropriate size and by optimizing the suspension stability, it is possible to observe an increase in the thermal conductivity of nanofluids, which do not follow the classical Maxwell's theory [3].

E. Effect of Nanoparticle Concentration on Thermal Conductivity

The last experiment of the present study investigates the effect of the nanoparticle concentration on the thermal conductivity. It is conducted using different volume fractions of Al_2O_3 as mentioned in Table VIII. Fig. 14 shows the results of this experiment.

TABLE VIII
EXPERIMENTAL CONDITIONS (CONCENTRATION EFFECT)

Diameter of nanoparticles (nm)	50
Volume fraction of Al_2O_3	0.25 – 0.5 – 0.75 - 1 and 2 Vol.%
Weight fraction of SDBS	0
pH	5.7
Ultrasonication	12 h for 500 ml **20** min for each 50ml
Temperature	25 °C

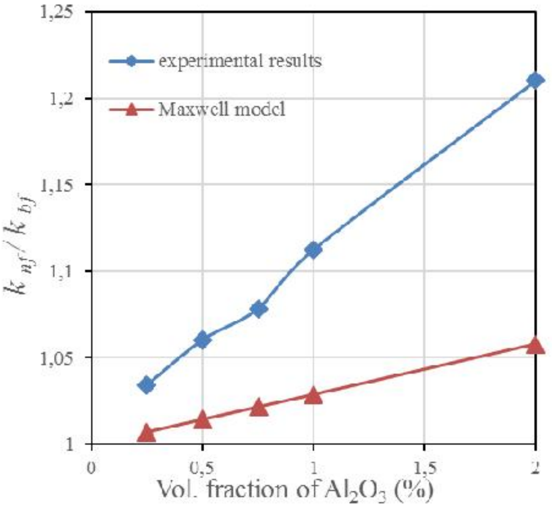

Fig. 14 Evolution of the thermal conductivity ratio with the volume fraction of Al_2O_3

As seen in Fig. 14, when the concentration of nanoparticles increases, the ratio of the thermal conductivity also increases. An enhancement of 21% is observed for a 2% concentration. Compared to the Maxwell model [3], which uses microparticles, one can see that there is a strong improvement using nanoparticles. This allows us to validate once again the utility of nanofluids comparing to micro- or milli-sized ones.

IV. CONCLUSION

In this paper, the thermal conductivity enhancement of Al_2O_3-water nanofluids was investigated under different pH values and different SDBS dispersant concentrations. The effect of these two parameters was identified by direct measurements of the conductivity based on the THW method. The stability of nanofluids has a direct influence on the thermal conductivity. Better preparation conditions lead to the higher thermal conductivity of nanofluids. The optimization of the pH value and SDBS concentration can result in the highest thermal conductivity of the nanofluids. Hence, the isolated and combined adjustment with both the pH and surfactant concentration was found to increase the thermal conductivity of nanofluids. Improving nanofluids can be done by optimizing different parameters such as pH value and SDBS concentration, but also by changing the particle size and particle concentration in the base fluid. Therefore, after identifying the optimal preparation conditions, both effects of size and particle concentration on the thermal conductivity were examined.

The major challenge of this work was the stability of nanofluids, as the suspension tries always to agglomerate. as well as fixing an optimal protocol to conduct the different experiments. By establishing an experimental protocol allowing the control of the parameters and the separation of their effects, the impact of each factor was studied and the different outcomes are presented in the following:

- Adding SDBS surfactant causes the variation of pH as well as the thermal conductivity. Moreover, the conductivity cannot be well improved by adjusting the SDBS concentration when the pH value is not in the optimal range.
- Adding surfactant does not necessarily enhance the thermal conductivity and in some cases, a degradation of the thermal conductivity is observed using surfactant.
- pH is the key parameter for stabilizing nanofluids. The variation of the thermal conductivity with the pH is not linear and the optimal value ranges for the three particle sizes i.e. 50, 135 and 200 nm between 5.4 and 5.8. For these values and without addition of surfactant, an increase of the conductivity of more than 20% can be observed with 50 nm/2 Vol.% mixtures. This level of enhancement was not reached with the use of the SDBS at random pH values.
- The optimal SDBS concentration for 50 nm size was found to be 0.01 wt.% with a fixed pH at 5.7.
- The maximum enhancements of the thermal conductivity are 21.7%, 14.2% and 11.7% for 50 nm, 135 nm and 200 nm respectively for a fixed nanoparticle concentration of 2 vol.%.
- Thermal conductivity improves decreasing the size of particles.
- Thermal conductivity improves when the particle concentration in the base fluid increases and the maximum enhancement for 50 nm size is found to be 21.7% at 2 vol%.

Finally, one can conclude that by using appropriate measurement techniques and by optimizing the preparation conditions, it is possible to observe an increase in the thermal conductivity of nanofluids, much higher than the one predicted by the classical Maxwell’s theory [3].

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