

## Nanoparticle concentration and ultrasonic treatment effects on surface tension of ZnO-water nanofluids

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### ABSTRACT

Applications of nanomaterials require thorough consideration of surface phenomena to understand in which ways nanomaterials differ from their conventional counterparts. Nanofluids attracted attention for potentially improved heating and cooling performance due to their enhanced thermal conductivity. Surface tension (ST) is another property that is highly worthy of research, as it reflects in bubble formation during phase change heat transfer, as well as in a variety of droplet-based applications. In this work, ST of ZnO-water ( $\varphi = 0.05\text{--}0.4$  vol.%) nanofluids prepared via two-step method was investigated experimentally, dependent on direct ultrasonication amplitude (40% and 100%) and ultrasonication period (0.5-4 minutes). Results showed that ST of ZnO-water nanofluids depend on nanoparticle fraction and ultrasonication parameters in a non-monotonous fashion, such that optimum ultrasonication parameters were present maximizing or minimizing ST as the application necessitates. It is necessary to consider the effect of temperature of the liquid when interpreting ST of nanofluids after ultrasonication.

Keywords: Nanofluid, ZnO nanoparticles, Surface tension, Ultrasonication.

### 1. Introduction

As the miniaturization trend is shining on engineering devices due to potential of higher efficiency, higher reproducibility, and lower operation cost; understanding how materials behave at the nanoscale has become essential. Shrinking sizes of heat transfer systems/paths has made thermal management units of small-scale devices more challenging. Nanofluids have the potential to improve thermal performances (and thermal management) by combining improved surface to volume ratio of nanoparticles compared to larger ones, and higher thermal conductivity of some metallic and nonmetallic solid particles, compared to those of conventional heat transfer liquids. The literature on nanofluids is mostly focused on thermal conductivity and heat transfer coefficient of nanofluids. On the other hand, surface tension (ST) as a temperature dependent property that is present in case of a discontinuity between densities of a liquid and its surrounding is a critical property in many applications including boiling heat transfer, thermosyphons, heat pipes [1], condensation [2], and spray cooling [3] along with product formation for nano-biomedical applications. Therefore, understanding on how nanofluids surface tension ( $ST_{nf}$ ) changes with process conditions is of great importance.

However, limited research have been performed on this property of nanofluids. Moosavi et al. [4] measured the ST of ethylene glycol (EG) based ZnO nanofluids containing ammonium citrate as a surfactant (with a surfactant-to-nanoparticle ratio of 1:1). The average ZnO particle size was  $\sim 67$  nm. The  $ST_{nf}$  measurements conducted according to the ring method have shown that the ST ratio ( $ST_{nf}/ST_{bf}$ ) increased as the nanoparticle concentration increased up to 3%. Wanic et al. [1] measured  $ST_{nf}$  of EG based nanofluids with AlN, Si<sub>3</sub>N<sub>4</sub>, TiN nanoparticles of 0.01, 0.025, and

0.05 mass fractions via du Noüy ring method and pendant drop method. Their results showed that  $ST_{nf}$  did not depend strongly on nanoparticle size, morphology, surface area, and concentration. Tanvir and Qiao [5] measured the  $ST_{nf}$  of water, ethanol, and n-decane based Al, Al<sub>2</sub>O<sub>3</sub>, B, and MWCNT nanofluids using pendant drop method. They concluded that  $ST_{nf}$  increased with nanoparticle concentration after a critical value, below which it had a little influence, except for MWCNT nanofluids. Chinnam et al. [6] measured  $ST_{nf}$  of propylene glycol & water (60:40) based Al<sub>2</sub>O<sub>3</sub>, ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> nanofluids of varying concentrations at different temperatures. They concluded that at constant temperature  $ST_{nf}$  decreased as nanofluid got more concentrated. This phenomenon was explained by the fact that increased number of nanoparticles attracting more liquid molecules towards them (and away from the surface), thereby reducing  $ST_{nf}$ . Murshed et al. [7] measured temperature dependent  $ST_{nf}$  of water based TiO<sub>2</sub> nanofluids within 25-55°C. They reported that  $ST_{nf}$  decreased as the temperature increased, while the  $ST_{nf}$  was lower than that of water at all the temperatures considered.

One major concern for nanofluids industrial application is colloidal instability. Ultrasonication has been a viable process to re-assure nanoparticles dispersion in host medium and is shown to affect nanofluid properties, such as thermal conductivity and viscosity ([8], [9]). Although it is an essential process, the effect of ultrasonication on the surface and interfacial tensions of nanofluids were not reported in the literature, to the best of the authors knowledge. This work aims at reporting on  $ST_{nf}$  of ZnO-water nanofluids dependent on nanoparticle concentration and ultrasonication parameters. A more detailed discussion on ultrasonication dependence of  $ST_{nf}$  of ZnO-

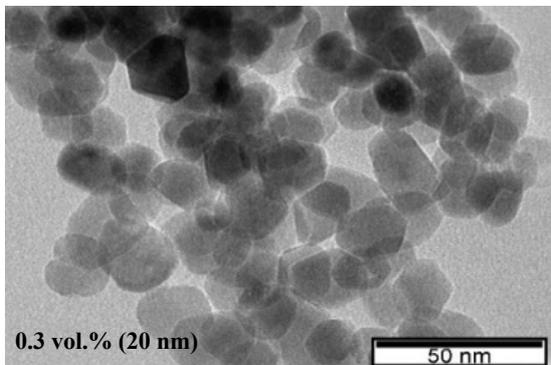
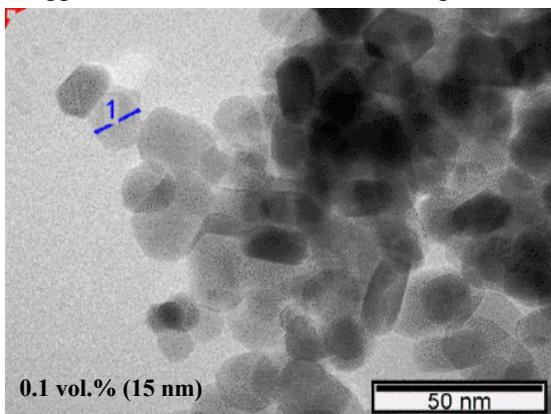
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water nanofluids with in-depth statistical analysis is recently presented by the authors [10].

## 2. Materials and Methodology

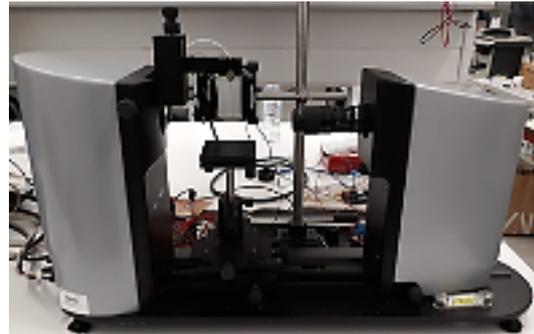
ZnO nanopowders (i.e., Zn (II)oxide powders) used in this study were obtained from IoLiTec Nanomaterials, Germany. The primary average particle size and shape provided by the manufacturer were 20 nm and spherical. However, a Transmission Electron Microscopy (TEM) imaging study was performed for the morphological characterization of nanoparticles. From TEM images analysis of nanofluids at different concentrations (Fig.1) it was found that the primary particle sizes are close to the value provided by the manufacturer (20 nm). TEM images also confirm that the nanoparticles have nearly spherical or polygonal shape. Furthermore, Fig.1 also demonstrates that nanoparticles form agglomerates inside base fluids and agglomeration increases with increasing concentration.



**Fig.1** TEM images of ultrasonically untreated ZnO-water nanofluids.

Then sample nanofluids were prepared by two-step method by mixing the necessary amount of ZnO nanoparticles in distilled water. The concentration of nanoparticles was from 0.05 to 0.4 volume % ( $\phi$ ). The mixture was then stirred using a magnetic stirrer for up to 30 minutes to ensure that nanoparticles had enough kinetic energy to participate in the dispersion. No surfactant or dispersant was used in this study. Direct (probe) ultrasonication has been considered as more effective compared to indirect (bath) ultrasonication in terms of reducing the agglomeration [11]. Therefore, in this work,

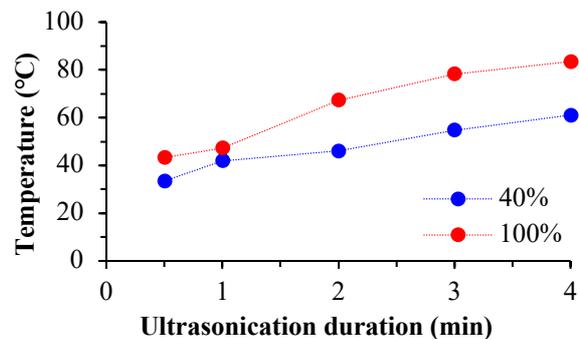
after stirring, sample nanofluids were treated via direct ultrasonication (Hielscher UP200Ht) for up to 4 minutes, at 40% or 100% ultrasonication amplitudes. ST measurements were performed using an Attension Theta Optical Tensiometer (Fig. 2) by pendant drop method. The syringe containing the sample was cleaned thoroughly with distilled water and using manual air pumping before and after every measurement. For each case, ST of 5 different droplets from the same stock were measured. Data were taken right after the droplet was stably dispensed out of the syringe to eliminate droplet vaporization.



<b>Measurement method</b>	Pendant drop method
<b>Analysis mode</b>	Young-Laplace
<b>Droplet volume</b>	5 $\mu$ L
<b>Temperature variation</b>	No

**Fig.2** Photograph of the tensiometer used for ST measurements (top) and table summarizing experiment details (bottom).

Before measurements of  $ST_{nf}$ , preliminary experiments using water was performed, revealing an experimental error of 1.23%. In experiments, no intentional temperature variation was induced on the samples, although ultrasonically treated samples temperature raised by the ultrasonication process. For the sake of comparison, temperature of the base fluid was also measured after direct ultrasonication at the same conditions as the nanofluid samples were treated. Fig. 3 shows the considerable increase in temperature of base fluids as an indication of how ultrasonication at 40% and 100% amplitude affects sample temperature.

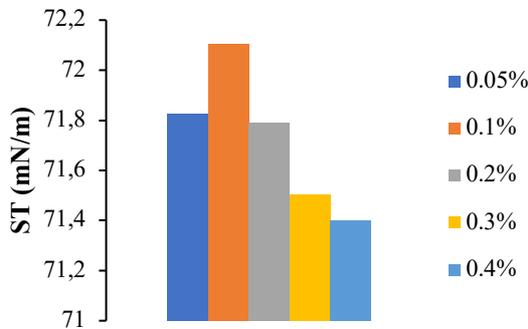


**Fig.3** Temperature increase of the base fluid with ultrasonication at two amplitudes.

### 3. Results and Discussion

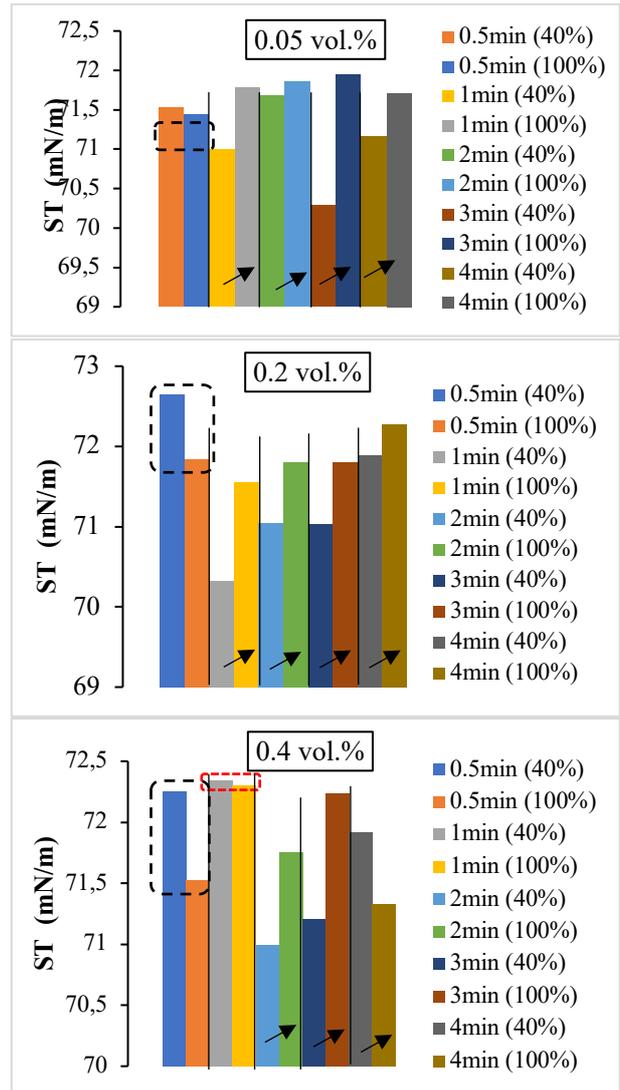
ST variation with nanoparticle concentration is shown in Fig. 4. These data were collected without any intentional temperature variation since these samples were not ultrasonicated. Results reveal that following the initial increase of  $ST_{nf}$  from 0.05 to 0.1 vol. % concentration,  $ST_{nf}$  decreased with nanoparticle concentration for 0.1-0.4 vol. %. The  $ST_{nf}-\phi$  relation does not show a strong and monotonous dependence, as the standard deviation of the data is  $\sim 0,28$  with the arithmetic mean of  $\sim 71,73$  mN/m.

When it comes to ultrasonicated nanofluids, the  $ST_{nf}-\phi$  relation implicitly involves the temperature effect, as ST of the base ( $ST_{bf}$ ) fluid strongly depends on temperature. In this regard, interpretation of ST behaviour requires consideration of  $ST_{bf}$  – temperature relation. For an objective interpretation a relative ST is defined, as  $ST_r = ST_{nf}/ST_{bf}$ .



**Fig. 4**  $ST_{nf}$  - nanoparticle concentration relation for ultrasonically untreated ZnO-water nanofluids.

Fig. 5 shows the  $ST_{nf}$  results individually for three nanoparticle volumetric concentrations (0.05%, 0.2 and 0.4%), in a comparative manner, dependent on ultrasonication duration and amplitude. The results presented in Fig. 5 include the implicit effect of temperature ( $T$ ), besides the ultrasonication amplitude and duration.  $T$  effect on ST of liquids ( $ST_{bf}$ ) is well-developed. Since direct ultrasonication results in  $T$  increase of nanofluid samples, especially for longer durations and/or higher amplitude, the  $ST_{nf}$  results reflect  $T$  variations. Fig. 5 also reveals that, for the same concentration,  $ST_{nf}$  of samples ultrasonicated at 100% amplitude were generally greater than those treated at 40% amplitude, except for the 0.5 min processes. This shortest period of ultrasonication provided an initial decrease in  $ST_{nf}$  for 0.05% and 0.2% samples while for 0.4 vol.% sample did not reveal an increase of  $ST_{nf}$  for 1 min and 4 min ultrasonication when 100% amplitude is compared to 40% amplitude. Nonetheless 100% amplitude typically provided greater  $ST_{nf}$  compared to those obtained after 40% amplitude for the same duration (Fig. 5).



**Fig. 5** Duration dependence of  $ST_{nf}$  of different concentrations of ZnO nanofluid at two different ultrasonication amplitudes (% in the parentheses).

Fig. 6 reveals that  $ST_r$  of nanofluids ultrasonicated at 100% amplitude are greater than  $ST_r$  of those ultrasonicated at 40% amplitude. In other words,  $ST_{nf}$  of samples ultrasonicated at 100% amplitude rises faster than  $ST_{nf}$  of those ultrasonicated at 40% amplitude. The  $ST_r$  increases with ultrasonication duration for both amplitudes, while the  $ST_r$  variation caused by the ultrasonication duration is much more pronounced for 100% amplitude when compared to 40% amplitude. These results demonstrate a direct link between ST and the homogeneity/dispersion level of nanoparticles in the based fluids.

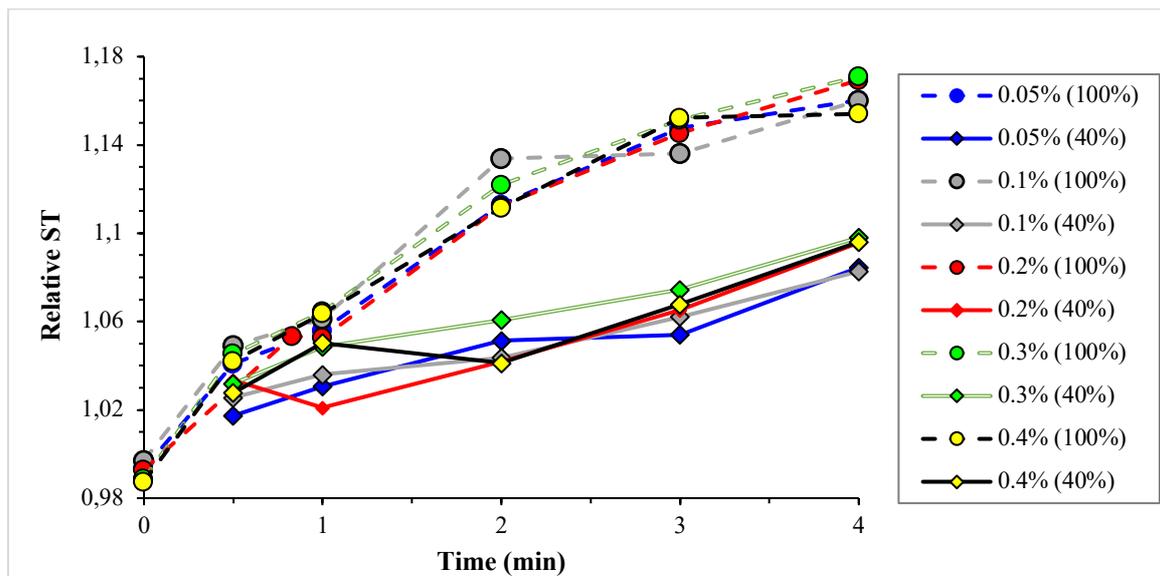


Fig. 6  $ST_r$  – ultrasonication time relation for ZnO-water nanofluids.

#### 4. Conclusions

By focusing on ZnO-water nanofluids ST behaviour, it is concluded that  $ST_{nf}$  depends directly on the level of colloidal stability. For surfactant free ZnO-water nanofluids, ultrasonication is a must to improve nanoparticle dispersion, and it strongly impacts the  $ST_{nf}$  and  $ST_r$ . Probe ultrasonication can be fine-tuned to obtain desired ST values by investigating intermediate ultrasonication amplitude and ultrasonication durations, or alternatively ultrasonication power. Tuning  $ST_{nf}$  via ultrasonication is a viable option, as it allows adjusting  $ST_{nf}$  without manipulating nanoparticle or base fluid amount. Consideration of samples temperature variations during probe ultrasonication is required when interpreting the variations not only in ST but also in temperature-dependent properties of the nanofluids. Findings of this study can also be useful for preparation of any types of nanofluids and their properties characterization.

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