

# Effects of Critical Temperature on the Stability and Lifespan of Air Nanobubbles

Nachael George Mwanga\*, Salum Kamota\*\*

\* College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China

\*\* State Key Laboratory of Pollution Control and Resource Reuse, Tongji University, Shanghai 200092, PR China

DOI: 10.29322/IJSRP.14.04.2024.p14828

[10.29322/IJSRP.14.04.2023.p14828](https://doi.org/10.29322/IJSRP.14.04.2023.p14828)

Paper Received Date: 22nd March 2024

Paper Acceptance Date: 24th April 2024

Paper Publication Date: 30th April 2024

## Abstract

The existing studies have yielded valuable insights into the temperature-dependent behavior of bulk nanobubbles in aqueous solutions, emphasizing the role of bubble pressure, surrounding temperature, and surface charge that facilitates random movement and repulsion mechanisms which prevents coalescence leading to the formation of bigger unstable bubbles. However, there remains a significant gap in understanding the specific impact of temperatures near critical points, such as the freezing point of water, on the stability and existence of nanobubbles. Unraveling nanobubble's response under extreme temperature conditions, particularly near phase transitions of their surrounding medium is crucial for comprehending the underlying mechanisms governing their stability. To address this gap, our research focused on investigating the behavior of bulk nanobubbles near the critical points of water. We employed nanoparticle tracking analysis to assess bubble distribution, size, and concentration changes with varying temperatures, aiming to provide essential insights into their existence and stability mechanisms. Our findings revealed that nanobubbles persist even at 0°C, albeit with a decrease in concentration and an increase in size. These results carry significant implications for industrial applications such as cryogenics, thermal processes such as cooling, manufacturing of lightweight materials, and environmental remediation where temperature may affect the nanobubbles-aided process.

**Index Terms-** Bulk nanobubbles, Critical temperatures, Nanobubble stability.

## I. INTRODUCTION

Nanobubbles are minuscule gas-filled cavities in a liquid. They have a small size which measures less than 100 nm. [1]. The significance of nanobubbles lies in their ability to facilitate processes such as water treatment for enhanced gas transfer and pollutant removal [1, 2], assist in food and beverage processing for improved product quality [3], medical applications like drug delivery systems and diagnostic techniques [4], and improving nutrient absorption in agriculture for enhanced plant growth [5]. At the core of nanobubbles' effectiveness in various applications lies their exceptional stability in water. Unlike

traditional bubbles that have high rising velocities, nanobubbles experience Brownian motion due to their highly negatively charged outer surface, facilitating repulsion between bubbles and preventing coalescence [6]. Therefore, it will take a significant amount of time for the nanobubble to rise to the surface. Nanobubbles have high internal pressure due to their tiny size that can be estimated using the Laplace equation ( $\Delta P = 2\gamma/r$ ), where  $\Delta P$ ,  $\gamma$ , and  $r$  denote the additional pressure, surface tension, and radius of the nanobubble, respectively. According to Epstein and Plesset's equation, NBs should disappear quickly into the liquid due to how they're formed and how pressure affects them [7]. The theory predicts that a bubble with a starting size of 1000 nanometers should vanish in less than 0.02 seconds. However, many experiments show the opposite [8, 9] Their existence and stability even after extended periods have been proved using many techniques [10, 11]. The resistance of NBs against diffusion and shrinkage can be explained by many theories. One is that NBs are stable due to the accumulation of negative charges [12], unusual surface tension or density on the nanoscale [6], surface-polarization interaction [13], and the adhesion of contaminant molecules at the interface between liquid and gas [14]. As the EP theory explains the stability equilibrium can only be reached when there is another counter force acting outwards to prevent the collapse of the bubbles. The two models that possibly explain the counter force are the electric double layer (EDL) model and the dynamic equilibrium model. The former model suggests that, an electric double layer around them stabilizes nanobubbles (NBs). which can be imagined as a protective electric shield. The electrostatic repulsion generated by the negatively charged surface of a bubble could counterbalance the Laplace pressure resulting from surface tension [15]. The dynamic equilibrium model suggests that the hydrophobic materials in water repel the water near their surfaces rusting in depletion layer formation which significantly reduces the density of water that results in trapping of gas dissolved in water causing the higher elevated amount of gas at the area. This inward diffusion balances the outward flow of gas from the uncovered part of the bubble, preventing it from shrinking further [16]. For NBs to maintain their stability, the temperature of the surrounding liquid has a greater influence as it affects the surface tension, gas solubility, and diffusion rates.

Several studies have been carried out to investigate the impact of

Parameter	Value	Measuring instrument
pH	7	Mettler Toledo (Five Easy Plus)
Conductivity ( $\mu\text{s cm}^{-1}$ )	4	Toledo (Five easy plus)
Temperature ( $^{\circ}\text{C}$ )	25	Mettler Toledo
Turbidity (NTU)	1	Hach (2100Q)

temperature on the existence and stability of bubbles [6, 17]. However, there is a notable gap as these studies did not extensively explore the behavior of nanobubbles (NBs) after exposure to critical temperatures, such as near freezing point where water transitions from liquid to solid phase. This research endeavors to fill this void by designing experiments that examine the effect of such critical temperatures on NBs. The study focuses on determining the size, concentration, and distribution of nanobubbles using the nanoparticle tracking analysis technique.

## II. METHODOLOGY

### A. Nanobubbles water preparation.

Nanobubbles were generated using 2 liters of deionized water produced by a molecular purifier machine. The nano scientific micro-generator model LF-02PT, which can generate microbubbles ranging from 0.01 to 456 micrometers, was used to produce the bubbles through the hydrodynamic cavitation method. The airflow rate was set at 10 mL per minute, and saturated water was released at a pressure of 0.65 MPa. The water flow rate was maintained at 1300 mL per minute under standard conditions.

Table 1. Characteristics of Water.

### B. Samples preparation

Room-temperature bubbled water was chilled in a refrigerator until it reached  $-2^{\circ}\text{C}$  under atmospheric pressure

## III. RESULTS AND DISCUSSIONS

### A. The effects of temperature on dissolved oxygen

The results from Figure 2. illustrate the impact of temperature on dissolved oxygen (DO) concentration levels in water for bubbled and un bubbled water. Initially, at room temperature, the presence of nanobubbles significantly increased the amount of dissolved oxygen compared to water without bubbles. This phenomenon occurs due to the large surface area of micro and nanobubbles, which enhances the oxygen transfer efficiency from the bubbles to the water. However, as the temperature decreased, the solubility of oxygen in water also decreased, leading to a decline in DO concentration for both bubbled and un-bubbled water. The lowest DO levels are observed at  $14^{\circ}\text{C}$ , indicating reduced oxygen solubility as temperature drops.

conditions. Throughout the cooling process, samples were collected at every two-degree interval as the temperature dropped. This procedure was repeated three times, and the averages of the measurements were noted. Following this, the experiments were replicated with a reverse approach, this time starting from  $-2^{\circ}\text{C}$  and gradually increasing the temperature. The bubbled water was first frozen in the fridge and then thawed, with temperature measurements taken at two-degree increments during the warming phase, mirroring the cooling procedure as it can be well illustrated in Figure 1.

### C. Measurement of Nanobubbles

The size, concentration, and distribution of bulk nanobubbles were determined using the nanoparticle tracking analysis (NTA) technique. Zeta View machine model PMX-130-12J-R5 was used and the data were analyzed through Software Zeta View (version 8.05.16 SP3). The technique works by utilizing light scattering and Brownian motion monitoring to analyze nanobubbles. A laser beam is directed through the sample, where the nanobubbles in water scatter the directed beam of light. This scattered light is then observed through the objective lens of a microscope. The NTA software subsequently tracks the Brownian motion exhibited by the NBs, allowing for the calculation of their diameters based on the Stokes-Einstein relationship for Brownian motion. This method provides a more accurate measurement of size distribution and concentration compared to other methods such as dynamic light scattering (DLS) and it has been used in many studies [18, 19].

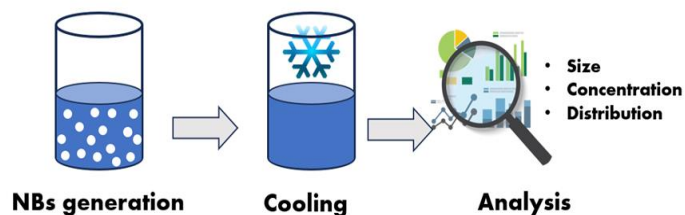


Figure 1. Experimental procedures.

Interestingly, as the temperature drops further, the DO concentration starts to rise again for both types of water. This

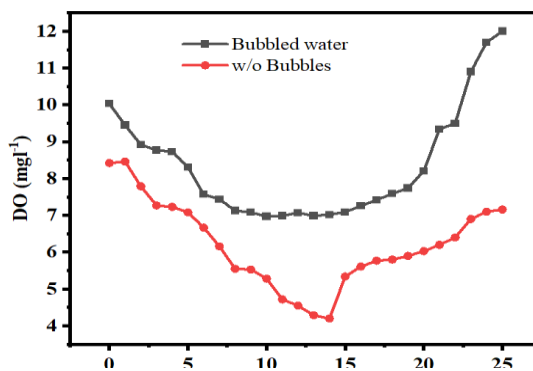


Figure 2. Concentration of dissolved oxygen plotted against decreasing temperature.

increase can be attributed to the fact that colder water can hold more dissolved gases, including oxygen, leading to higher DO levels despite the reduced solubility at lower temperatures. The amount of dissolved gas in water determines the size and concentration of bubbles formed during cavitation and the dissolution rates after bubble production.

**B. Effect of temperature on bubble concentration**

Figure 3. shows the results of NBs concentration in response to temperature change whereby, at temperatures near room temperature, the concentration of nanobubbles fluctuated without showing a consistent trend. This lack of stability in concentration suggests that the condition of water around room temperature did not affect the stability of nanobubbles in a specific direction. However, as the temperature dropped to 14 °c and continued to decrease, the concentration of nanobubbles began to rise steadily. This increase in concentration can be attributed to the lower temperature creating conditions that are more conducive to the formation and preservation of nanobubbles. At around 4 °c, the concentration peaked at around 9.9E+6 particles mL<sup>-1</sup>, indicating that this temperature range is particularly favorable for nanobubbles stability, resulting in the highest observed concentration. At 4°c water experiences maximum density which increases the molecule's stability by reducing molecular movement. Conversely, when the temperature dropped further to 0°c, the concentration of nanobubbles declined. This decrease could be due to water undergoing a phase transition from liquid to solid and becoming ice. During this transition, the arrangement of water molecules changes. Further freezing could lead to bubbles disappearance as has been reported by N Nirmala., etl [20].

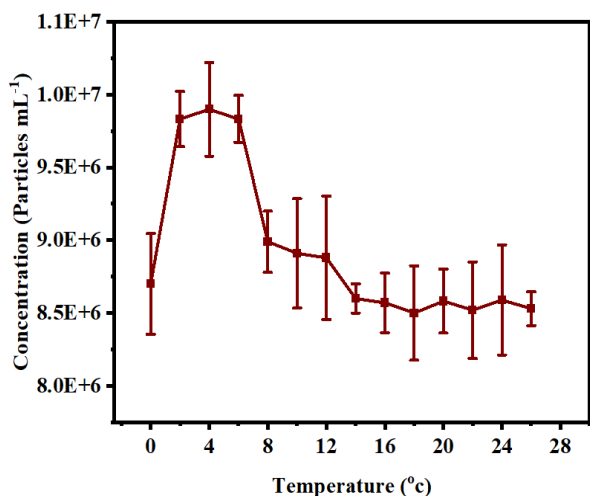


Figure 3. Relationship between bubbles concentration and temperature decrease.

**C. Effect of temperature on the nanobubble size**

The size of nanobubbles demonstrated a clear response to temperature variations. Figure 3 illustrates this by depicting an increase in nanobubble size from room temperature up to 19°c. This size increase suggests that lower temperatures promote the

growth of nanobubbles, leading to larger bubble sizes. However, between 20 °c and 12 °c, the size of nanobubbles exhibited fluctuations, showing a trend of decreasing sizes. This fluctuation could be due to the effect of temperature on gas pressure with low temperature leading to lower pressures that affect the compression of the gas bubbles, making them smaller and more stable. The most significant change in nanobubble size was observed around 4 °c, where the size decreased notably to 146 nm. This decrease in size could be attributed to the influence of viscosity as water experiences maximum density at this temperature, as discussed earlier, the more viscous water is the less movement of molecules occurs. This phenomenon might result in smaller and more stable nanobubbles. An increase in surface tension due to a decrease in temperature might have exerted a stronger force on the nanobubbles, causing them to contract and reducing their diameter. Interestingly, as the temperature dropped further to 0 °c, the size of nanobubbles began to increase again, reaching 176 nm. This increase in size at very low temperatures could be influenced by factors such as reduced molecular movement and increased gas solubility, leading to the growth or aggregation of bubbles. Overall, the results indicate that the size of nanobubbles is sensitive to changes in temperature, with lower temperature ranges facilitating expansion and increase in bubble size.

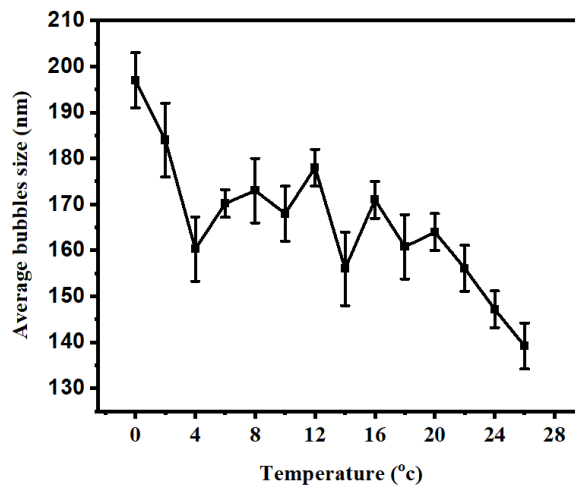


Figure 4. Average nanobubble size plotted against temperature decrease.

#### D. Bubbles distribution

Figure 5. shows the distribution of nanobubble's size with respect to their volumes. At room temperature, nanobubbles exhibited a broader range of size distribution. This phenomenon was attributed to the heightened molecular movement which occurs when higher temperature decreases the water density and viscosity in allowing easy movement of molecules. Conversely, as the temperature decreased, the distribution of nanobubbles also declined. At 0°C, the range of nanobubbles distribution narrowed, concentrating bubbles within a smaller size spectrum. Cold temperatures resulted in reduced thermal energy in the water, causing the gas molecules inside nanobubbles to lose kinetic energy. This loss of energy contributes to the contraction of the nanobubbles and the decrease in their diameter distribution. Despite the increased gas solubility and concentration with decreasing temperature, this shift in distribution highlighted the significant impact of temperature on nanobubble distribution. Lower temperatures led to a more concentrated size distribution among the bubbles compared to higher temperatures.

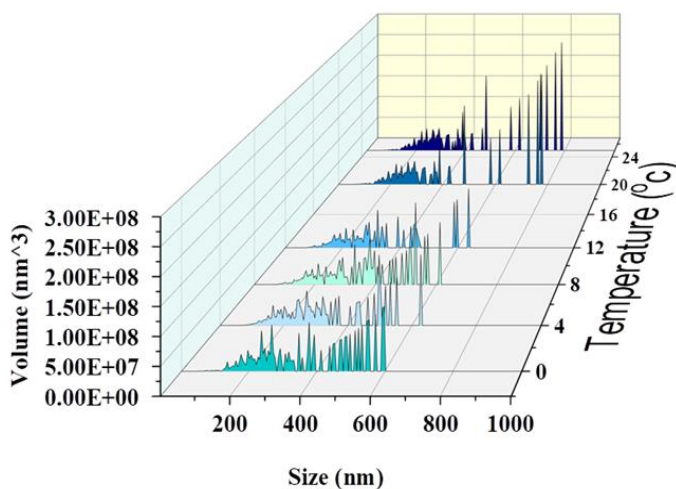


Figure 5. Volume distribution plotted against size and temperature.

#### IV. CONCLUSION

The study investigated how critical temperature impacts the properties and stability of nanobubbles, leading to the following conclusions:

- Temperature changes influence the amount of dissolved oxygen in water, with bubbled water showing the same sensitivity compared to non-bubbled water. Lower temperatures showed the ability to hold more oxygen compared to warmer water.
- The concentration of nanobubbles fluctuates more at temperatures close to room temperature and increases rapidly at 4°C, where water reaches its maximum density.

- The density of bubbled water affects the size and concentration of nanobubbles whereby as cooling approached the high density of water which is 4°C, the average size of bubbles decreased to about 160 nm.
- Temperature exerts a substantial influence on the distribution of nanobubbles. Higher temperatures resulted in a broader distribution range, while lower temperatures led to a narrower distribution range.
- Bubbles persist even after reaching 0°C which is a critical temperature, demonstrating their remarkable stability even under such critical conditions.

#### REFERENCES

- [1] W. H. Shen et al., "Microbubble and nanobubble-based gas flotation for oily wastewater treatment: a review," *Environmental Reviews*, 2022, doi: 10.1139/er-2021-0127.
- [2] I. Levitsky, D. Tavor, and V. Gitis, "Micro and nanobubbles in water and wastewater treatment: A state-of-the-art review," *Journal of Water Process Engineering*, vol. 47, 2022, doi: 10.1016/j.jwpe.2022.102688.
- [3] Z.-H. Zhang et al., "Micro-nano-bubble technology and its applications in food industry: A critical review," *Food Reviews International*, pp. 1-23, 2022, doi: 10.1080/87559129.2021.2023172.
- [4] M. H. Luo, C. K. Yeh, B. Situ, J. S. Yu, B. C. Li, and Z. Y. Chen, "Microbubbles: A Novel Strategy for Chemotherapy," *Curr Pharm Des*, vol. 23, no. 23, pp. 3383-3390, 2017, doi: 10.2174/1381612823666170113092148.
- [5] A. K. A. Ahmed et al., "Influences of Air, Oxygen, Nitrogen, and Carbon Dioxide Nanobubbles on Seed Germination and Plant Growth," *J Agric Food Chem*, vol. 66, no. 20, pp. 5117-5124, May 23 2018, doi: 10.1021/acs.jafc.8b00333.
- [6] J. Meegoda, S. Aluthgun Hewage, and J. Batagoda, "Stability of Nanobubbles," *Environmental Engineering Science*, vol. 35, 09/26 2018, doi: 10.1089/ees.2018.0203.
- [7] M. S. Plesset and S. S. Sadhal, "On the stability of gas bubbles in liquid-gas solutions," *Journal of Chemical Physics*, vol. 18, pp. 1505-1509, 1950.
- [8] D. Lohse and X. Zhang, "Pinning and gas oversaturation imply stable single surface nanobubbles," (in eng), *Phys Rev E Stat Nonlin Soft Matter Phys*, vol. 91, no. 3, p. 031003, Mar 2015, doi: 10.1103/PhysRevE.91.031003.
- [9] B. H. Tan, H. An, and C. D. Ohl, "Stability of surface and bulk nanobubbles," *Current Opinion in Colloid and Interface Science*, p. 101428, 2021.
- [10] S. Zhou et al., "The effect of preparation time and aeration rate on the properties of bulk micro-nanobubble water using



- hydrodynamic cavitation," *Ultrasonics Sonochemistry*, vol. 84, p. 105965, 2022/03/01/ 2022, doi: <https://doi.org/10.1016/j.ultsonch.2022.105965>.
- [11] F. Eklund, M. Alheshibri, and J. Swenson, "Differentiating bulk nanobubbles from nanodroplets and nanoparticles," *Current Opinion in Colloid & Interface Science*, vol. 53, p. 101427, 2021/06/01/ 2021, doi: <https://doi.org/10.1016/j.cocis.2021.101427>.
- [12] A. Khaled Abdella Ahmed et al., "Colloidal Properties of Air, Oxygen, and Nitrogen Nanobubbles in Water: Effects of Ionic Strength, Natural Organic Matters, and Surfactants," *Environmental Engineering Science*, vol. 35, no. 7, pp. 720-727, 2018/07/01 2017, doi: 10.1089/ees.2017.0377.
- [13] M. R. Ghaani, P. G. Kusalik, and N. J. English, "Massive generation of metastable bulk nanobubbles in water by external electric fields," *Science Advances*, vol. 6, no. 14, p. eaaz0094, 2020, doi: doi:10.1126/sciadv.aaz0094.
- [14] K. Yasui, T. Tuziuti, W. Kanematsu, and K. Kato, "Dynamic Equilibrium Model for a Bulk Nanobubble and a Microbubble Partly Covered with Hydrophobic Material," *Langmuir*, vol. 32, no. 43, pp. 11101-11110, 2016/11/01 2016, doi: 10.1021/acs.langmuir.5b04703.
- [15] K. Yasui, "Mechanism for Stability of Ultrafine Bubbles," *JAPANESE JOURNAL OF MULTIPHASE FLOW*, vol. 30, no. 1, pp. 19-26, 2016, doi: 10.3811/jjmf.30.19.
- [16] K. Yasui, T. Tuziuti, and W. Kanematsu, "Mysteries of bulk nanobubbles (ultrafine bubbles); stability and radical formation," *Ultrasonics Sonochemistry*, vol. 48, pp. 259-266, 2018, doi: 10.1016/j.ultsonch.2018.05.038.
- [17] M. Li, X. Ma, J. Eisener, P. Pfeiffer, C.-D. Ohl, and C. Sun, "How bulk nanobubbles are stable over a wide range of temperatures," *Journal of Colloid and Interface Science*, vol. 596, pp. 184-198, 2021.
- [18] J. Gross, S. Sayle, A. R. Karow, U. Bakowsky, and P. Garidel, "Nanoparticle tracking analysis of particle size and concentration detection in suspensions of polymer and protein samples: Influence of experimental and data evaluation parameters," *European Journal of Pharmaceutics and Biopharmaceutics*, vol. 104, pp. 30-41, 2016/07/01/ 2016, doi: <https://doi.org/10.1016/j.ejpb.2016.04.013>.
- [19] V. Filipe, A. Hawe, and W. Jiskoot, "Critical evaluation of Nanoparticle Tracking Analysis (NTA) by NanoSight for the measurement of nanoparticles and protein aggregates," *Pharmaceutical research*, vol. 27, pp. 796-810, 2010.
- [20] A. W. P. N. Nirmalkar, and M. Barigou, "On the Existence and Stability of Bulk Nanobubbles," vol. 34, pp. 10964-10973, 2018, doi: 10.1021/acs.langmuir.8b01163.

#### AUTHORS

- First Author** – Nachael George Mwanga. Master's degree in environment, Tongji University  
**Second Author** – Salum Kamota. Master's degree in environmental science, Tongji University.