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The Physics of Nanobubbles

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ABSTRACT

The interesting subject of gas nanobubbles has attracted great attention of many scientists due to their extraordinary and “mysterious” properties. Nanobubbles are a scientific challenge due to their special properties such as very small size, very large surface-to-volume ratio, high internal pressure, rapid adhesion to hydrophobic surfaces, and long-term stability on a time scale. Due to these unique properties, diverse applications of nanobubbles have been developed in many fields of science and technology such as chemical, biological, materials, and medical industries. Despite theoretical considerations that predict that spherical gas bubbles cannot reach stable equilibrium, various experiments demonstrate the existence of stable nanobubbles which can be survived during several hours or even days. Can it be proven that nanobubbles exist and, if so, how can they survive? Given the importance and variety of applications of nanobubbles, it is essential to review recent advances in nanobubbles and their stability mechanisms. This article summarizes the latest scientific studies on the properties of nanobubbles. We believe that the results of this study will help researchers to understand nanobubbles better and more deeply and pave the way for future studies by researchers.

INTRODUCTION

Nanobubbles (NBs) are defined as very small cavities filled with gas and their size ranges from tens to several hundred nanometers. These ultra-fine bubbles have attracted great attention because of their extraordinary physicochemical characteristics which make the nanobubbles different from micro bubbles and macro bubbles (ordinary bubbles). Unlike macroscopic bubbles, nanobubbles are a scientific challenge because of their unique properties such as their small size, extremely large surface to volume ratio, large internal pressure, longevity, rapid adhesion onto hydrophobic surfaces, and staying stable over a long period of time. These features have expanded the applications of bubbles of nanoscopic dimensions in a wide variety of scientific and technological fields including chemical, biological, material, and also medical industries. Many researchers have turned their attention to the fascinating topic of nanobubbles thanks to their great, unexpected, and ‘mysterious’ properties. Recently nanobubbles have presented important applications in biomedicine, environmental purification, wastewater or groundwater treatment, surfactant-free cleaning, mining, agriculture, mineral flotation, energy systems, the food industry, increasing metabolism in animals and plants, removing contaminants from soils, and in many other environmental and biomedical areas [1-12].

NBs are classified into two categories based on their morphology and locations: Surface nanobubbles that located at the solid-liquid interface in the form of spherical capped or pancake bubbles with lateral dimensions of a few microns and a height of several nanometers, and bulk nanobubbles that are spherical bubbles (100 to 200 nm) that are suspended and freely dispersed in the bulk liquid. The extraordinary longevity of different type of nanobubbles is known as the most peculiar characteristic of them [1,5,10,13-14].

Gases dissolved in water tend to accumulate at the interfaces between water and hydrophobic solids to form cap-shaped surface nanobubbles or interfacial nanobubbles. These nanobubbles are observed on different substrates and their unusual stability is studied using different theoretical models. Surface nanobubbles are mysterious and unknown in two ways. First, according to theoretical considerations, they are expected to dissolve within a few seconds, while observations show that they can remain stable for a few minutes to even several days. Secondly, there are differences between the contact angles of nanobubbles with hydrophobic surfaces. The existence and stability of surface nanobubbles were established following various experimental, analytical and simulation

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studies by different researchers. Interfacial nanobubbles have attracted researchers' attention because of their implications for different technical applications and interfacial phenomena, such as long-range attractive forces between hydrophobic surfaces in solutions, the stability of colloidal systems, liquid slippage at hydrophobic walls, and bio-molecular adsorption. Also, they are effective in bubble formation at the solid/water interface as gas micronuclei. [1,2,15-17].

Bulk nanobubbles are a novel class of nano-scale bubbles with unexpected properties. In fact, bulk nanobubbles are nanoscopic spherical gas domains which form stable colloids in supersaturated solutions due to dissolving an excess of gas into solution. Diffusion of dissolved gases and production of buoyant nanobubbles lead the escape of gas from the supersaturated solution. Initially, the existence of bulk nanobubbles was proposed in 1981 by Johnson and Cooke. They found that wind-generated bubbles in seawater can last for about a day or even longer due to the existence of membranes created by surfactants. They also observed that by changing the external pressures applied to the small bubble, its size is affected, so that the negative pressure leads to bubble expansion and the positive pressure causes it to deflate, and a large increase in the positive space causes the bubble to disappear. This compressibility confirms the gaseous state of the materials inside the nanobubbles. Some other scientist believe that salt water can prevent bubbles from coalescing. Breaking waves in seawater results in the formation of many small bubbles which persist for up to 24 hours. After the report of bulk nanobubbles by Johnson and Cook up to 1990s, when Bunkin et al investigated the presence of stable microbubbles in diluted electrolytes, little information was available on bulk nanobubbles. But in recent decades, numerous articles have been published on bulk nanobubbles. In bulk 2000, the interesting properties of bulk nano-scale bubbles like their long lifetime and very high pressure inside the bubbles were proposed according to the Young-Laplace equation. In summary, based on numerous experiments, it is confirmed that the bulk nanobubbles are indeed filled with gas. In the last decade, many scientists have investigated the existence of ultrafine bubbles suspended in pure water experimentally. Also, there are many computational modeling investigations on bulk nanobubbles.

However, the nature of nanobubbles is still mysterious, and a large number of questions remain unanswered, generally related to their composition, stability, and mechanisms of formation. Despite recent studies, some researchers continue to speculate about the reality and durability of bulk nanoscale bubbles. A theory was presented by Epstein−Plesset for prediction the lifetime of a bubble, which depends on its radius and saturation in 1950. Based on this theory, the bubble is expected to dissolve within 10 microseconds. But researchers' reports indicate the stability of bulk nanobubbles for hours, days, or even months. There are two explanations for the long-range stability of bulk nanobubbles. First, because of the small buoyancy force, the bulk nanobubbles are prevented from going up to the free surface and their movement is controlled by Brownian motion. The latter is the stability of bulk nanobubbles versus dissolution [4,9,10,13,15,18-23]

The 'very small nanobubbles' are at the center of an industry that the Wall Street Journal valued at US$10 billion in 2020. It is forecasted that nanobubble technology growing market share, reaches €145 M in EU up to 2030. Recently, a report suggests very broad applications with a multi-billion dollar market [5,24].

Considering the importance and diversity of nanobubbles application, it is necessary to review the recent advances in nanobubbles, and also discuss their stability mechanisms. The main aim of this article is to present a summary of the latest scientific findings about the properties of nanobubbles. We believe that the results of this study will help researchers to understand nanobubbles better and deeper.

The physics of nanobubbles

Composition of Nanobubbles

Essentially, the gas nanobubbles are consistent with two parts of an inner core (central gas) and an outer layer (stabilizing shells), each of which has its own physical and chemical characteristics. Core constitutes the main part of the volume of a nanobubble and is a low-density chamber. Different usages of fine-bubbles can be achieved by changing the gas inside the core. For instance, in order to increase the lifetime and stability of nanobubbles, perfluorocarbons and sulfur hexafluoride can be used in combination with O_2. Due to the density of the gas and aqueous solution around the nanobubbles, the application of acoustic waves causes them to oscillate. The shell is formed as a shielding layer around the gas and acts as a barrier for gas diffusion between the enclosed gas and the aqueous environment. The shell is mostly composed of surfactants, polymers or proteins, and its composition plays a significant role in the stiffness of the bubbles, the tear tolerance in the presence of ultrasound effects, and the ease of their detection. For example, soft shells crack quickly, while hard shells cannot vibrate even in ultrasonic environments. Shell structure is determined by factors such as density, half-life, elasticity, gas exchange and resistance to applied ultrasonic pressure [8].

Do nanobubbles really exist?

Considering the production methods and a wide range of application of nanobubbles, it may be surprising that the academic intrigue over ultrafine bubbles is that "Do nanobubbles really exist? if they exist, how they can survive. The existence and stability of ultrafine-bubbles was a controversial and mysterious issue until recently. This debate was raised in 2007 when the journal Nature published the article "No Nanobubbles" in its "Research Highlights" section [5,25].

From 1950, where Epstein−Plesset's theory was presented up to 2000, few papers had been published on nanobubbles. But recently, the number of publications and citations related to nanobubbles is fast increasing yearly. In the literature, there are convincing experiments for the existence and stability of surface bubbles. Some articles have disputed the existence of bulk nanobubbles without providing any definitive direct or indirect evidence. In contrast, more than 200 articles have been reviewed that report indirect experimental and/or theoretical verification for the existence, sustainability, or applications of bulk ultrafine-bubbles in various fields [14-15,26-28].

One of the basic questions is whether it is possible to produce stable bulk nanobubbles in water by cavitation or adding organics into water, which creates a barrier at the gas/water interface. Another question that arises is that when producing bulk nanoparticles in pure water, these nanoparticles actually are nanoparticles or they are solid nanoparticles separated from the adjacent surfaces. Many researchers doubt whether the nanobubbles observed in the mixture of water and organic liquids are really nanobubbles or supramolecular structures and refer to nanobubbles as nanobodies. Some researchers, based on their experimental investigations, believe that NBs can be formed mainly on the hydrophobic surface of a solid and they are able to have an influence on interfacial properties like surface forces and lubrication absorption and also stabilize the colloidal particles. Rak et al. in claimed that there are no bulk nanobubbles. They have investigated the effect of ultrasound cavitation and addition of ethanol into water on the stability of nanobubbles in detail and they have reported that both of these factors can produce nano-objects. According to their studies, very small metallic nanoparticles are produced from the surface decomposition of the metallic probe of the ultrasonic device. Furthermore, a population of nanoparticles/nanodroplets can be created by adding organic solutes to water, which arises from the dissolution of hydrophobic materials that there are in the added solutes. However, in 2020, Jadhav et. al. while discussing the concept of bulk nanobubbles and presenting evidences such as IR, nanobubble encapsulation, TEM analysis, Raman spectroscopy, cryo SEM analysis, and ICP-MS analysis stated that bulk nanobubbles not only exist, they also have long-term stability in nature. According to their reports, Cryo-SEM images show nano-entities as cavities and the value of dissolved gas is related to the amount of nanobubbles produced [7,26].

In 1994, Parker et al. [25] presented the first report about the existence of bubbles by a very sensitive force-measuring system. They found that the force of attraction between two hydrophobic surfaces in water is dependent on the distance between the surfaces. They considered this phenomenon related to the presence of surface nanobubbles.

In fact, nanobubbles increase the force of attraction by filling the gap between surfaces. After conducting experiments, they estimated the height of nanobubbles to be less than 100 nm. Although this report was presented in a situation where theoretical studies were against the existence of stable nanobubbles, this study was able to relate the existence of bubbles to hydrophobic attractive force between hydrophobic surfaces in an aqueous medium. Observing the Tyndall effect using a laser beam is considered as one of the first evidences for the existence of NBs. Furthermore, the advanced tools such as dynamic light scattering, high-resolution light microscope, confocal laser scanning microscope, and cryo-EM microscopes enable the evaluation of nanobubble size [28].

According to traditional theory, it is predicted that the existence of clean bulk nanobubbles is difficult. An opinion about gas diffusion in bubbles presented by Epstein and Plesset in 1950. They assumed that the bubble exists in isolation at rest and neglected the boundary motion of a bubble as it expands or contracts. Before studying gas diffusion, the concentration of the gas in the solution containing the bubble must be determined near and far from the bubble. The first case can be determined by Henry's law, and the second case can be determined based on the amount of dissolved gas in the solution. The lifetime of bubbles bigger than 1 μm is reported to be according to observations. But the theoretical lifetime of bubbles smaller than 1 micrometer is under 0.02 seconds. Although, many scientists are not sure about the existence of bulk nanobubbles for days, there are experiments that confirm the existence of bulk nanobubbles ranges from several hours to weeks, which are several times longer than theoretical predictions. Effects on water purification and surface cleaning indirectly indicate the fact that bulky nanobubbles do exist. Due to the paradox between theoretical and observational results, it's very important to understand the existence or absence of contaminated bulk nanobubbles using novel analysis methods [4].

Classical thermodynamic theory predicts that nanobubbles cannot remain stable, and based on calculations bubbles with 100 nm in radius will only present in water for around 10 microseconds. Initial studies on long-range interactions between hydrophobic species indicates the existence of nanobubbles at the solid-liquid interface. The existence of a long-range attractions, which was notably greater than the intermolecular forces, between hydrophobic species immersed in water has been determined. Later, the range of action of this long-range attraction has been determined to be 10-100 nm [29].

Nanoparticles or nanobubbles? In several experiments, unwanted contaminants can scatter light, and detection tools are not able to distinguish contaminants from small bubbles. Therefore, nanoparticles might be mistaken for nanobubbles. In some researches in 2010, dispersion of nanoparticles in water and organic solvents was observed, which was appear after degassing. These particles were most presumably organic pollutants, not nanobubbles. In 2019, the influence of impure ethanol on bulk nanobubbles was studied. They observed many fine particles in the liquid (1010 per milliliter of sample). But when the ethanol was purified, the nanoparticles disappeared and ultra-light microscopy cannot determine the particles [4].

After the observation of the nanobubbles using an atomic force microscope (AFM), the researchers' report indicated the fact that the existence or absence of nanobubbles is related to the history of the liquid. It is an important result, because it could explain why some researchers have been able to observe nanobubbles while others cannot see evidence of bubbles in similar systems. It has been observed that with the presence of nanobubbles on the surface, the hydrophobic attraction force goes up. Furthermore, nanobubbles can be formed by immersing the hydrophobic surface in water, whereas no nanobubbles are observed if the surface is hydrophilic at first and becomes hydrophobic during chemical reactions in the absence of air. In fact, nanobubbles are simply formed on hydrophobic surfaces and stick to them more strongly [25]. The fact that some pollutants have been mistaken for bulky nanobubbles has led researchers to question the validity of the classical Epstein-Plast theory. Further studies are needed to answer the question of whether the classical Epstein-Plast theory is still valid at the nano-scale.

Nanobubbles Stability

The remarkable longevity of bulk NBs is known as their most unique characteristic. Based on the experimental studies while microbubbles have been observed to exist for only seconds, the NBs have a lifespan of hours, days or months. Although the existence of bulk nanobubbles was confirmed experimentally a certain theory of their enigmatic longevity and stability has not been accepted yet. Bulk nanobubbles smaller than 1 µm might be survive for a long period of time, because Brownian motion can negate the buoyancy force. However, based on the classical Young-Laplace theory, the surplus internal pressure predicts their rapid collapse. Bubbles are thermodynamically unstable due to the energy cost of the interfaces. When the bubbles coalescence either at the surface or with other bubbles, the overall interfacial area of the bubbles decreases. Also, squeezing the gas inside the bubble reduces the surface area and the size of the bubble. Obviously, decreasing the bubble size increases the pressure inside the bubble. Formation of micro and macro bubbles is controlled by Young–Laplace equation which can also describe the relationship between the pressure of a spherical bubble and its immediate surrounding as following [12,18,24,28]:

$$\Delta P = \frac{2\gamma}{R} \tag{1}$$

$$\Delta P = P_{vap} - P_{liq} \tag{2}$$

The Laplace pressure (ΔP) is the pressure difference of the inside and outside of a bubble where the P_{vap} and P_{liq} are the pressure of vapor phase (inside the bubble) and liquid phase (outside the bubble), respectively, and R is the radius of bubble. The molecular interaction between the gas center and the liquid can be determined by the surface tension (γ) at the interface of binary compounds. According to equation (1) the inner gas pressure for bubbles can be estimated. Therefore, based on the Epstein–Plesset theory the nanobubbles could be dissolved on a time scale of milliseconds. One can be seen from this equation, Laplace pressure is inversely proportionate to the radius of a bubble, and smaller bubble has higher internal pressure that could be especially higher in the case of nanobubbles. As the bubbles shrink and the internal gas escapes from the core, the Laplace pressure increases. Surface tension causes a pressure which can dissolve bubble by gas diffusion [7,8,15,18]. The Henry's law describe the dissolution equilibrium between the gas inside the bubbles and surrounding liquid [14] as equation (3), where H and c are the Henry constant and the gas concentration in the liquid, respectively. Also, P is the pressure inside the NB:

$$H = \frac{c}{P} \tag{3}$$

An important question is how are gas nanobubbles able to withstand internal pressures without dissolving in solution? The interface of a bubble isn't impermeable and allows the movement of gas and vapor molecules from solution to bubble and contrariwise. The net flow rate of a gas can be obtained using the solvability of the gas and the dissolved gas in the liquid. Temperature and pressure affect gas solvability. Gas solubility versus pressure is proportionate to the partial pressure of the gas and is expressed by Henry's law. The inside of a bubble has more pressure than the surroundings, and its value depends on the radius of the bubble. The internal pressure is higher for smaller bubbles. This increase in pressure increases the solvability of the gas forming the bubble in a solution. As a result, the gas escapes from the bubble by diffusion and dissolves in the liquid. The escape of gas from the bubble reduces the size and increases the pressure inside the bubble and establishes equilibrium (Young-Laplace equation). This cycle can cause rapid dissolution and disappearance of fine bubbles. The bubbles with a millimeter radius which are kinetically stable, this effect is small, but according to this theory the microbubbles should disappear within tens of milliseconds [25]. Macrobubbles can rise to the surface faster than macrobubbles and burst. Microbubbles rise to the surface more slowly and due to the greater transfer of gas from the bubble to the liquid, become smaller after a few hours and eventually disappear. The swelling/shrinkage properties of microbubbles and nanobubbles are different from macrobubbles. In 2013, Li et al. [30], have reported that the critical size separating bubble swelling and shrinkage is ~50 to 65 µm. The bubbles smaller than this critical diameter shrink, while larger bubbles swell. Based on the experimental study by Takahashi, microbubbles gradually get smaller and finally vanish because of long stagnation and dissolution of inner gas into the surrounding solution, while nanobubbles tend to survive in the liquid for several weeks [31]. According to this study, smaller bubbles with higher zeta potential remain for longer time in the solution. Because fine bubbles motion of small bubbles is governed by both the buoyancy force and Brownian motion. The random motion leads to a continuous diffusion of gas within the bubble and the bubble become smaller and finally disappear. Based on the research, with time the radius of bubble goes up while the magnitude of zeta potential reduces. This is due to the bubbles coalescing over time and consequently growing in size. Hence, as the surface charge density of the nanobubbles decreases due to diffusion, the nanobubbles become smaller in size and eventually disappear like microbubbles [23].

In 2021, Zhou et al discussed the relation between stability of bulk nanobubbles with more different parameters such as the bubble radius, the temperature, and the chemical potential difference between the gas of the bubble and the solution. They have found that a perturbation of the diameter of the bubble causes its dissolution or unlimited growth. They believe that the bulk nanobubbles are thermodynamically unstable and a necessary condition to have a stable nanobubble is:

$$\frac{d(\Delta P)}{dR} > 0 \tag{4}$$

This is a key result to understand the stability of nanobubbles and suggests that a stable bulk nanobubbles can be expected if the Laplace pressure radius curve presents a positive slope. Here, it has been suppose that the surface tension between the gas and solution interface is constant, then equation (4) is surely negative. If the surface tension is influenced by the radius of bubble, Eq. (4) may be satisfied.

Several mechanisms have been suggested for the surface tension of bubbles which are depending on radius. Based on Tolman effect, if we can compare the size of the bubble to the scale of the intermolecular forces, then the surface tension will depend on the size of the bubble. This effect is important only for those bubbles about 1 nm in size, while, the experiments showed that the nanobubbles are generally 100 nm. There is another possible mechanism that firstly was suggested by William Ducker in 2010 for explanation of the stability of surface nanobubbles [32]. This mechanism arises from the sorption of trace amounts of pollutants in solution, which can be trapped at the interface because of their hydrophobic properties. The surface density of the contaminants increases by dissolution of the bubble. Therefore, the interfacial area decreases making the surface tension of bulk nanobubbles size related. Recently this mechanism has been modified by scientists to clarify the stability of nanobubbles. Some surfactants are insolvable in water and can pin at the surface after adsorption. The surface tension decreases by decreasing the gas/water interface area, as demonstrated by many investigations on Langmuir films. It is well known that by absorption of irresoluble surfactants at the interface, bubble stability can be notably increased [14]. In fact, the stability of nanobubbles is dependent to some factors such as surfactant structure and surface polymers, size and low density gas in the center of the nanobubble, which are coated and stabilized by materials like lipids and polymers. In addition, at the interface affecting the bubble, the gas phase can act as a surfactant. Negative surface charge and high internal pressure cause long-term stability of nanobubbles in liquids with high concentrations. Scientists are presenting different hypotheses that indicate the stability of nanobubbles [7]. Tan et al. [33] reported that the charges located at the gas/water interface causes the stabilization of bulk nanobubbles. Then, the effective Laplace pressure describes by equation (5):

$$\Delta P = \frac{2\gamma}{R} - \frac{Q^2}{32\pi^2 R^4 \varepsilon} \tag{5}$$

where Q and ε are the total charges pined on the interface and the dielectric coefficient of the solution, respectively. The charges adsorbed on the surface of bubble can be obtained by the zeta potential of the microbubbles. Also, the stability of bubble at different gas saturation conditions is presented.

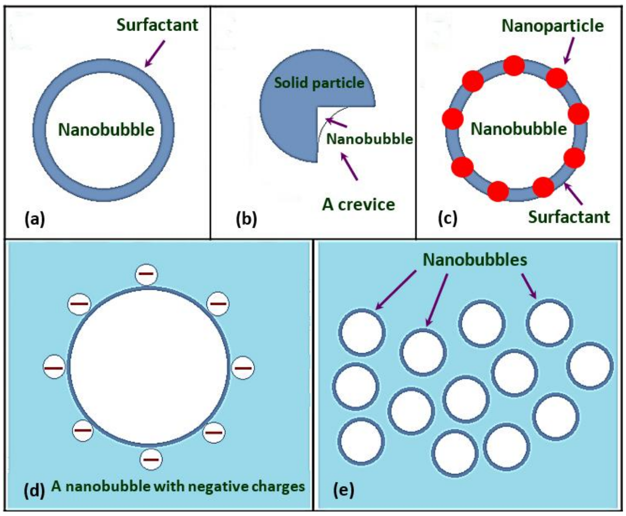

Fig. 1. Different models on the stability of bulk nanobubbles (a) skin model, (b) particle crevice model, (c) armored bubble model, (d) electrostatic repulsion model (a negatively charged nanobubble with radius R, in a liquid with pressure P0. The pressure inside the nanobubble, P is: $P = P_0 + 2\frac{2\sigma}{R} - \varepsilon\frac{\zeta^2}{R^2}$ which σ is surface tension and ζ is potential, (e) many body model (a liquid supersaturated with nanobubbles).

To date, different models have been reported to clear the stability of nanobubbles [5,34-38]. Some researchers have linked the relatively long lifetime of bulky nanobubbles to the effects of different pollutants adsorbed on the surface of the bubbles or to local saturation. Yasui et al., 2018 [39] proposed a number of stabilization models for bulk nanobubbles, such as the skin model (dependent on the effect of organic materials), Figure **1**(a) [4,40], the particle gap model (due to the influence of a concave gas-liquid interface, Fig. 1(b), the "armored" bubble model (related to the effect of surfactants and solid nanoparticles, Fig. 1(c), the electrostatic repulsion model (corresponding to the mutual repulsion of surface charges, Fig. 1(d) [41] and the many-body model (associated with the influence of many nanobubbles, Fig. 1(e) [42]. Each model is only able to explain a part of the observed phenomena and does not agree with many other phenomena, and therefore these models cannot fully explain the stabilization of bulk nanobubbles [4]. The results of the researchers shows the materials attached to the surface of bubble has little influence on the lifetime of the bubble and is depending on the contact angle. Temperature also shows a weak influence on the lifetime of the bubble. If the solution becomes supersaturated with gas, the feedback cycle employs inversely and small nuclei growth fast to form bubbles. The lifetime of small bubbles does not depend on surface tension [25]. Based on some recent studies [43-45] a main factor for stabilization of bulk nanobubbles is the selective adsorption of negative electrical charges at gas–solution interface. The charged surface can prevent bubble joining together and balances the Laplace pressure. Therefore, the gas diffusion into the solution is prevented. A negatively charged interface causes the zeta potential to become negative. According to the searches in the literature, not many reports were found explaining the effect of temperature on the value of zeta potential. Based on the researches, in the case of air bubbles in ionic solution of surfactant the zeta potential would be zero by increasing temperature [46]. This could be because when temperature goes up, the adsorption of surfactant molecules on the surface of bubble might decreases resulting reduction of surface charge density. In colloidal liquids, the zeta potential generally arises from the chemisorption of ions on the particle surface. It has been reported that the temperature influence on zeta potential is complicated, and related to the potential or ionic distribution, charging characteristics, and sorption equilibrium [9,47-48].

The theory of electrostatic repulsion is the most popular theory about the stability of NBs [49]**.** There is an electrostatic repulsion force at the gas-water interface because of the negative charge of gas-water interface [18,50]. Electrostatic repulsion and van der Waals attraction can specify the stability of colloidal liquids. Derjaguin, Landau, Verwey and Overbeek (DLVO) theory [51] could explain the colloidal stability. Researchers have shown that nanobubble surface in pure water has negative charges and an electrical double layer is organized around the nanobubble. The ions located around the surface of bubbles create a thin layer which prevents diffusion and reduces gas dissolution and thus increases the lifetime of nanobubbles. This effect is known as ionic shielding. The external electrostatic pressure exerted by the charged nanobubble interface helps balance the internal Laplace pressure and leads to stability of the nanobubble [52]. The hydrogen bonding model is another important theory [53] which based on differential hydrogen bonding at the interface of gas and water plays an important role in the stability of nanobubbles. In the case of nanobubble the length of hydrogen bond is 0.27 nm instead of 0.3 nm, and it reduces the surface layer of gas diffusion. It was experimentally confirmed that the transfer rate of gas from bubble to solution reduces when water is gas supersaturated [54,55]. Another accepted theory which arises from this fact is the super-saturation theory. This theory suggests that the stability of NBs is related to the low gas dissolution rate in the surrounding liquid medium, which was gas supersaturated. According to other theories such as dynamic equilibrium model [39] and skin model [56], solid materials play a role in the stability of NBs. In the theory of dynamic equilibrium, it is supposed that covering part of the surface of a NB with a hydrophobic material stabilizes it against dissolution. Water repellency by hydrophobic materials causes the formation of a depletion layer on the surface, and the gas is preferentially confined in the discharge layer. Therefore, the gas pressure on surface of the hydrophobic substance increases much more than the ambient pressure. According to another theory known as the skin theory, an organic skin completely covers the nanobubble surface. Therefore, diffusion of gas from inside the nanobubble to solution is completely prevented [24]. In fact, a surfactant acts as a diffusion barrier, will increase the stability of nanobubble by establishing a dynamic balance of gas flux at the interface [39,57]. A recent review has studied the effect of surfactants on nanobubbles [58].

The degree of stability for nanobubbles is related to the zeta potential. The nanobubbles stability goes up with increasing the zeta potential because of the repulsion between the bubbles. A reduction in zeta potential leads to less stability of nanobubbles and their coagulation. The value of Zeta potential of bulk nanobubble dependes on the electrolytes, surfactants, pH and gas type. In 2022, Alam et al have measured the zeta potential values between − 20 mV and – 30 mV, at a neutral pH [59]. Han and Bui et al [60,61] have reported that at pH between 4 and 12, the nanobubbles have negative charges. The influence of the gas type on zeta potential of nanobubbles has been experimentally studied by Meegoda et al. [62]. They have found that the zeta potential is associated with the solubility of gas and its diffusion rate. The highest magnitude of negative zeta potential is belong to Ozone followed by oxygen, air, and nitrogen which is related to the various ability of each gas to produce OH- ions at the nanobubbles surface [24].

The stability of bulk nanobubbles has been attributed to the polarization at the interface of gas-water by Ghaani et al. [63]. This unique interfacial structured molecular environment causes preferable water-molecule orientations leading in electric dipoles. A repulsive force is produced by interactions between molecular dipoles at the interface, dependent on the size of bubble, finally enough to balance the Laplace pressure. Vacha et al. [64] suggested a similar point of view which zeta potential could be attributed to interface polarization of bubble [18].

The effect of magnetic field on water

The influence of magnetic field on water solutions has been studied for decades. As follows from the literature data, the magnetic field can has an influence on water structure and change its physicochemical properties. The impact of magnetic field on water is still a controversial issue, and the mechanism of the magnetic field treatment is not unambiguous. There are different studies that focus on the impact of magnetic field on properties of water such as surface tension, specific heat, viscosity, refractive index, evaporation amount, infrared spectrum, heat capacity, melting temperature and boiling point of water. These effects are related to the magnetic field stabilizing hydrogen bonds of water. The properties of water are very important in many applications and the clarification of the effect of magnetic field on water properties is desired in both science and technology. A review article studied recent approaches to magnetic field effects. Water has polar molecules. When water passing through a magnetic field with various intensities and circulation periods, it become magnetized water. Changes in water properties by applying a magnetic field can have negative or positive effects. Magnetization can influence on the hydrogen bond and Van der Waal's forces that control the water structure. In fact magnetization can change the structure of water, decrease the linkage angle and enhancement the solubility. Magnetic fields can affect the physical properties of water by changing the size of water clusters [65-68].

Magnetic treatment of water was performed for different usages, including agriculture, industry, wastewater treatment, preventing the scaling of metallic surfaces, construction and enhancement the performance of concrete [68-69]. Mosivand et al. [70] have investigated the effects of 0.15 T and 0.5 T magnetic field on removal of antimony and lead from water. They have found that applying the magnetic field causes increasing in the removal efficiency at pH lower than 3. Also, it can be effective on bubble removal from the electrochemical cell. Holysz et al. showed the magnetic field can enhance the conductivity of water and reduce its surface tension [71]. One approache concerning the effect of magnetic field on water is the field impact on the hydrogen bonds of water [66]. The influence of a static magnetic field on the hydrogen bonds of water has been investigated by Cai et al. They have explained the magnetization mechanism of water according to both experimental and theoretical models and molecular dynamics simulation [72]. Chang and Weng [73] found that increasing the magnetic field ranges from 1 T to 10 T can lead to an increase in the quantity of hydrogen bonds by ~0.34%. Also, Hosoda et al. [74] found the strength of hydrogen bonds increases via delocalization of electrons in the molecules with hydrogen bond by applying10 T magnetic field. Liu et al. reported that applying the magnetic field could accelerate the degradation of organic substances of pulp and paper wastewater. According to their results increasing the magnetic fields from 0 mT to 900 mT leads to an increase in the pH of water to the climax firstly and afterwards reduces [75]. According to the surface tension, viscosity results, and H1-NMR measurements by Cai et al. [72] increasing the average size of the water clusters after magnetic treatment was observed. Also, the structure of water clusters, water properties, and the process at the solid-liquid interfaces changes by changing the external magnetic field.

Some scientist have studied the effects of magnetic field on water using Monte Carlo simulation. The results show an increase in the number of monomer water involving the tetrahedrality. When high magnetic fields apply, increasing the refractive index is attributed to increased hydrogen bond strength. They could show a memory of magnetization imprinted by external cyclic pulsed-electromagnetic field in water. Also, they studied magnetized nanobubbles in mineral water by applying a pulsed electromagnetic field 1.8 mT using a dynamic light-scattering method and AFM images. Based on their report 0.03 mT magnetization was found for more than one day. They proposed a possible structure for magnetized nanobubbles [69]. Wang et al. have investigated the effect of magnetic field on the partial physical properties of water. Their results show that the properties of tap water change by magnetic field treatment depending on the magnetization effect and magnetic field strength has a great effect on the magnetization. The magnetic field treatment can increase the evaporation amount and reduce boiling point and specific heat of water. The optimal magnetizing condition was found as the magnetic field strength of 300 mT. Their findings offered a facile approach for improvement of cooling and power generation efficiency in industrial applications [68]. Szcześ et al. reported the static magnetic field at dynamic states can affect on the water contact angle measured on the mica and glass surface and also changes the surface wettability. Magnetic field could strengthens or weakens the contact angle changes depending on the strength of magnetic field. Based on their results action time is larger for more hydrophobic surfaces [66]. Fujimura and Iino investigated about the influences of magnetic fields on surface tension of water-air interfaces in 2009. They examined the surface tension using surface wave resonance method with very high precision. According to their findings surface tension increases by about 1.8 ± 0.2 % at a magnetic field of 10 T [65]. Karkush et al. studied about the effects of magnetic fields with different intensities on the electrical and chemical properties of tap water. Their investigation involves water circulation for 24 h in different magnetic fields with intensities of 500 G, 1000 G, 1500 G, and 2000 G. They have found that the magnetization of water increases some positive and negative ions like Magnesium, potassium, sodium, chlorine, and SiO_2 and decreases calcium. Their results show that the circulation of water in the magnetic field can rises water alkalinity. Also, after magnetic treatment, the nucleation of calcium mineral and sulfate content decreases. They have reported that the enhancement of the geotechnical characteristics of swelling and soft soil through precipitation of calcite in pores is the main application of magnetic water which leads to an increase in the bond between soil particles causing its strength [67].

Poulose et al. found that magnetic field enhances evaporation of water in confined spaces. They have reported that a magnetic field can change the evaporation speed due to altering the isomeric ratio in the vapor. They also investigated a significantly improved effect of magnetic field on evaporation speed of water confined in a microfluidic channel. According to their research findings, the average rate of water evaporation in a microfluidic channel with a relative humidity of above 100% is much higher than in an open beaker with unsaturated vapor [76].

CONCLUSION

In summary, the present review includes a comprehensive literature review of the latest developments in ultrafine bubbles technology and addresses the key challenges concerning the formation, detection and characterization of nanobubbles. The following findings can be highlighted.

- Although a lot of great progresses in the study of bulk nanobubbles have been reported recently, it is still in its early stages and many questions remain unanswered generally related to their composition, mechanisms of formation, large internal pressure, long lifetime and long-term stability. It has been reported that the stability of nanobubbles in alkaline environment is greater than in acidic medium. The negative zeta potential can be increased by adding anionic surfactant. It also improves the electrostatic stabilization of bubbles which leads to generation of smaller and more stable nanobubbles because bubbles with a high negative charge tend to repel each other, causing the prevention of inter-bubble merging and aggregation.

- Bulk nanobubbles tend to interact with a variety of soft matter systems and change the surface charge of various nanoparticles.
- A discussion about the stability of nanobubbles was presented according to experimental results and information reported in different literature. Regardless of gas type, stable nanobubbles with high zeta potentials could be produced under a controlled gas flow with sufficient energy and pressure. Furthermore, it is possible to increase the stability of nanobubbles in a medium which can provide OH- ions on bubble surface with higher concentration. However, the quantity of bubbles per volume (bubble density) must be considered to prevent the coalescence of bubbles. However, the number of bubbles per unit volume (bubble density) should be considered to avoid the possible coalescence of bubbles. In fact, the decrease in zeta potential and the random movement of bubbles leads to the coalescence of nanobubbles and their size increase.

- Although several models were proposed to make clear the stability mechanism of bulk nanobubbles, no satisfactory explanation has yet been offered for their longevity and it is necessary that the future research focuses on understanding the stabilization mechanisms of nanobubbles produced using different techniques.

Data Availability Statement

No Data associated in the manuscript.

Conflicts of interest

There are no conflicts of interest.

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