The effect of ultrasound on bulk and surface nanobubbles: A review of the current status

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ABSTRACT

The generation, and stability of nanobubbles are of particular interest for fundamental research and have potential application in numerous fields. Several attempts were made in the literature to produce nanobubbles through acoustic cavitation. However, the generation and stability mechanisms of nanobubbles in the acoustic field are unclear. Here, we review the effect of ultrasound parameters on bulk nanobubbles and surface nanobubbles. On this basis, we discuss the proposed generation and stability mechanisms of nanobubbles from the perspective of transient and stable acoustic cavitation. Moreover, we propose some future research directions for a deeper understanding of the role of ultrasound in the generation and stability of nanobubbles.

1. Introduction

The application prospects of nanobubbles are very wide and include surface cleaning, coagulation, boundary slip, mineral flotation, microfluidics, agriculture, wastewater treatment, sewage treatment, medicine, etc. [1-4]. Nanobubbles include bulk and surface nanobubbles. Surface nanobubbles are described as spherical caps that are a few nanometers to tens of nanometers high and about 1 μm wide [5,6]. They are well studied in the literature and proven to be gas filled entities [7,8], although the origin of their stability is still in dispute [9-15]. On the contrary, there is no conclusive evidence that that bulk nanobubbles are indeed gas filled bubbles despite the numerous reports in the literature investigating their existence [16,17]. However, there is a strong evidence in the literature that the supersaturation of dissolved gas in these systems leads to the formation of objects on the order of 100 nm in diameter [18,19]. In this review, we will use the term bulk nanobubbles to refer to all studies on bulk nanobubbles regardless of their entities. Bulk nanobubbles are commonly defined as those with a diameter smaller than 1 μm [2,20]. Other terms used for bulk nanobubbles in the literature are ultrafine bubbles (determined by ISO international standardization).

One of the common methods that are reported to produce bulk nanobubbles are based on hydrodynamic and acoustic cavitation [1,18,21-23]. Several types of generators have been developed using the principles of membrane, the venture effect, swirl liquid flow, and pressurized dissolution (see Table 1). In addition, some researchers have reported that bulk nanobubbles can be generated by a 20 kHz probe-type US processor (AUTOTUNE SERIES 750 W and 1500 W model, Sonics & Materials) [23-25], a 20 kHz Vibra-Cell sonicator (Sonic & Material Instrument) [26], a 42 kHz Bransonic Ultrasonic Cleaner Model [27], a Langevin transducer with multiple frequencies (HEC45242M, Honda Electronics) [1], and a frequency of 40 kHz ultrasound (no manufacturer information) [28]. It has been found that the concentration of dissolved oxygen obtained in ultrasonic water is lower than that in pure water, which suggests that bulk nanobubbles may form in the dissolved air and be stable in the undersaturated gas state once they have formed [24,28]. It has been reported that, the long-term stability of bulk nanobubbles is due to the negative charge on the nanobubbles’ surfaces [24,29]. Further, hydrogen bonding interactions was reported to play an important role in the mechanism of bulk nanobubbles’ generation and...
should be studied in terms of the modification of the classical nucleation time, ultrasound frequency, and power) on surface nanobubbles. In generation of bulk nanobubbles in the most of published literature. 35 kHz ultrasound probe. Jadhav and Barigou [23] used tapping mode atomic force microscopy (TMAFM) and optical microscopy to monitor the presence of physical defect points, “water channels,” in surface nanobubbles generated through an ethanol with water experienced growth via rectified gas diffusion yet did not nucleate cavitation in the presence of a piezoceramic ultrasound transducer (undatim Ultrasonics, 515 kHz). Li et al. [48] compared studies by Nirmalkar et al. [24] and Mo et al. [28] were 820 and 175 nm, respectively. It is worth mentioning here that two different devices were used in these studies to measure the size of the nanobubbles. Thus, this might justify the variation in size but it does not explain why the size increased significantly in Cho et al. [26], and slightly in and Mo et al. [28]. The variation of the ultrasound transducer used by Yasuda et al. [1] has a different working principle from the ultrasound probes used by Nirmalkar et al. [24] and Mo et al. [28]. Therefore, the contradictory results between the published studies may be due to the differences in the types of ultrasound equipment, the ultrasound frequencies, the properties of the pure water, and the sizes of the time scales.

In addition, Cho et al. [26] found that the effective diameter of bubbles increased from 850 nm to 4250 nm when the ultrasonic time increased from 2 to 6 min. Mo et al. [28], observed that the average diameter of the formed nanobubbles slightly increased from ~100 nm to ~220 nm when the ultrasonic time increased from 0.5 to 10 min. The average diameters of bulk nanobubbles in pure water for Cho et al. [26] and Mo et al. [28] were 820 and 175 nm, respectively. It is worth mentioning here that two different devices were used in these studies to measure the size of the nanobubbles.

2. The effect of ultrasound parameters on bulk nanobubbles

2.1. Sonication time

Nirmalkar et al. [24] investigated the effects of sonication time (i.e., ultrasound energy input, 20 kHz, and 750 W power of ultrasound probe) on the properties of bulk nanobubble suspension. As shown in Fig. 1(a), the population of bulk nanobubbles increased significantly with increasing sonication time. Fig. 1(b) indicates that the diameter of bulk nanobubbles generated by ultrasound ranges from 10 to 600 nm. With the increase in sonication time (~10 min), the peak value of numbers of bubbles increased from 1.76 × 10^6 mL–1 to 2.69 × 10^6 mL–1, while the specific diameter corresponding to the peak decreased from 339 nm to 72 nm. When the sonication time was increased further (>10 min), the peak value of the peak number of bubbles significantly increased to ~8 × 10^6 mL–1, and the specific diameter ranged from 77 to 87 nm. In addition, Yasuda et al. [1] reported that the concentration of bulk nanobubbles presents an increasing trend with irradiation time for different ultrasonic powers and frequencies. However, as observed in Fig. 2, Mo et al. [28] reported that the nanobubble concentration in the bulk solution first increased and reached a maximum at approximately 1 min and then decreased gradually from 1 to 10 min (at 40 kHz and 300 W power of ultrasound probe). In their nanobubble suspensions, all the bulk nanobubbles were below 300 nm. At 1 min, the 100 nm nanobubbles reached a maximum and then decreased with the ultrasonic time. It is important to note that the ultrasound transducer used by Yasuda et al. [1] has a different working principle from the ultrasound probes used by Nirmalkar et al. [24] and Mo et al. [28]. Therefore, the contradictory results between the published studies may be due to the differences in the types of ultrasound equipment, the ultrasound frequencies, the properties of the pure water, and the sizes of the time scales.

2.2. Ultrasonic power

Ultrasonic power significantly affects the nanobubble generation process.Cho et al. [26] reported that the effective diameter of bubbles increased from 850 nm to 4250 nm when the ultrasonic time increased from 2 to 6 min. Mo et al. [28], observed that the average diameter of the formed nanobubbles slightly increased from ~100 nm to ~220 nm when the ultrasonic time increased from 0.5 to 10 min. The average diameters of bulk nanobubbles in pure water for Cho et al. [26] and Mo et al. [28] were 820 and 175 nm, respectively. It is worth mentioning here that two different devices were used in these studies to measure the size of the nanobubbles. Thus, this might justify the variation in size but it does not explain why the size increased significantly in Cho et al. [26], and slightly in and Mo et al. [28]. The variation of the ultrasound transducer used by Yasuda et al. [1] has a different working principle from the ultrasound probes used by Nirmalkar et al. [24] and Mo et al. [28]. Therefore, the contradictory results between the published studies may be due to the differences in the types of ultrasound equipment, the ultrasound frequencies, the properties of the pure water, and the sizes of the time scales.

Table 1

| Method                  | Pressurized gas | Nanobubble diameter (nm) | Apparatus                        | Ref.      |
|-------------------------|-----------------|--------------------------|----------------------------------|-----------|
| Membrane                | Yes             | 250 – 1000               | Membrane module and pump         | [32]      |
| Pressurized dissolution | Yes             | 230 – 280                | Pump, jet nozzle                 | [33]      |
|                         |                 | 120 – 250                | Compressed air filter, saturator | [22]      |
| Venturi effect          | No              | 83 – 550                 | Pump, static mixer, and venturi  | [34-37]   |
|                         |                 | 150 – 240                | tube (or eccentricity nozzle)    |           |
| Swirl liquid flow       | No              | 200 – 800                | Baffled high intensity agitator   | [39]      |
| Breakup effect          | Yes             | 304 – 518                | Reservoir, pump, splitter        | [40]      |

their extremely long stability [30,31]. However, there is no agreement in the literature on why bulk nanobubbles are stable, and therefore the stability of bulk nanobubbles remains unexplained.

Temperature changes and ethanol water are the most commonly used methods to produce surface nanobubbles [41,42]. The formation of nanobubbles or microbubbles on a solid surface immersed in water is dependent on surface heterogeneities [5,6]. There are many preexisting gas cavities on hydrophobic solid surfaces, which can be due to the presence of physical “defect points,” normally termed “water channels” or “water tracks,” on solid surfaces [43,44]. When gas cavities (nuclei) exist on a substrate surface, bubble formation can occur at fairly low levels of gas supersaturation [45]. Additionally, the gas nuclei on particle surfaces are typically nanoscale in size [46]. Brotchie and Zhang [47] reported that preexisting surface nanobubbles produced on the surface of freshly cleaved, highly ordered pyrolytic graphite (HOPG) by the exchange of ethanol with water experienced growth via rectified gas diffusion yet did not nucleate cavitation in the presence of a piezoceramic ultrasound transducer (undatim Ultrasonics, 515 kHz). Li et al. [48] compared preexisting surface nanobubbles generated through an ethanol-water exchange at the HOPG-water interface in the absence and presence of a 35 kHz ultrasound probe. Jadhav and Barigou [23] used tapping mode atomic force microscopy (TMAFM) and optical microscopy to monitor the gas adsorption on the patterns before sonication. They found that high intensity ultrasonic irradiation (20 kHz) induces the formation of an interfacial gas layer at the solid surface immersed in different liquid media (water saturated with different gases, such as argon, nitrogen, or carbon dioxide) by accelerating the adsorption of dissolved gas. In the case of surface nanobubbles, other effects that confer stability, such as pinning, have been proposed.

It is worth noting that ultrasound equipment was only used for the generation of bulk nanobubbles in the most of published literature. There are few studies on the effects of ultrasound parameters (sonication time, ultrasound frequency, and power) on surface nanobubbles. In particular, the effect of ultrasound parameters on surface nanobubbles should be studied in terms of the modification of the classical nucleation theory. In this article, we conducted a systematic review of the behaviors of nanobubbles under various ultrasound parameters. In addition, some directions for future research have been proposed.
**Fig. 1.** Bulk nanobubble suspensions generated in pure water at different sonication times: (a) bubble number density; (b) number of bubbles. The size measurement method used in this study was Nanoparticles Tracking Analysis technique. Data source: Nirmalkar et al. [24].

**Fig. 2.** (a) Nanobubble concentration with different ultrasonic times in ultrasonic water. (b) Detailed size distribution with different ultrasonic times in ultrasonic water. The size measurement method used in this study was Nanoparticles Tracking Analysis technique. Data source: Mo et al. [28].

**Fig. 3.** Effect of ultrasound power on concentration of nanobubbles in ultrapure water at 22 kHz. The size measurement method used in this study was Nanoparticles Tracking Analysis technique. Data source: Yasuda et al. [1].

**Fig. 4.** Effective diameters of bubbles in pure water when ultrasonic power varied at 1 min ultrasonic time and a 20 kHz ultrasound frequency of the ultrasound probe. ZetaPlus (Brookhaven Instruments Co., Holtsville, New York) was used to measure the size in this study. Data source: Cho et al. [26].
When the ultrasound frequency increased from 22 kHz to 1 MHz, the concentration of nanobubbles decreased significantly (see Fig. 6). Further, Yasuda et al. [1] reports that the mode diameter of bulk nanobubbles by ultrasound has a small dependence on frequency. However, Brotchie et al. [49] reported that with an increase in the ultrasound frequency, the mean value of the distribution decreases from 4 μm to 1.5 μm, and the distribution of bubbles (micron-scale) becomes significantly narrower (see Fig. 7). It is notable that the bubbles in the studies of Yasuda et al. [1] and Brotchie et al. [49] belong to nanobubbles and microbubbles, respectively. Thus, the different observations between Yasuda et al. [1] and Brotchie et al. [49] can be attributed to the difference in the sizes of bubbles.

### 2.4. Types of generation of acoustic cavitation

The main types of experimental configurations for the generation of acoustic cavitation used for the generation of bulk nanobubbles are horn-type [23-28] and bath-type [1,49]. As shown in Fig. 8 (a), an ultrasonic horn (ultrasound probe) is immersed in a liquid. An acoustic wave is radiated from a horn tip that is much smaller than the acoustic wavelength [43]. For bath-type ultrasound equipment, an ultrasonic transducer is attached to the outer surface of a liquid container (see Fig. 8 (b)). In addition, the ultrasonic transducer can be attached to the inner surface of a small closed box immersed in the liquid [51]. Commonly, a thin plate of piezoelectric material is used in combination with a vibration plate for high frequencies in the range of 100 kHz–1 MHz, which are widely used for bath-type ultrasound equipment [52]. Bolt-clamped Langevin-type transducers (BLT) are more suitable for low ultrasonic frequencies (20–200 kHz), which are widely used for horn-type ultrasound equipment [43]. Fig. 9 shows a comparison of the size distributions of nanobubbles generated by bath-type and horn-type ultrasound equipment at a similar frequency level. It was observed that bath-type ultrasound equipment can generate a higher concentration of nanobubbles with a relatively lower power as compared to horn-type ultrasound equipment. This is a preliminary comparison due to the differences of the water temperatures and the ultrasound frequencies between Fig. 9 (a) and (b).

### 2.5. Effect of ultrasound parameters on surface nanobubbles

The first images of surface nanobubbles recorded using atomic force microscopy (AFM) were published by Ishida et al. [53]. Since then, AFM measurement has been a very common method for the observation of surface nanobubbles. Li et al. [48] reported that surface nanobubbles are not generated after sonication pretreatment in pure water (see Fig. 10). This phenomenon can be related to the contact angle of the HOPG surface and the gas concentration of the water solution. The advancing angle of water on HOPG is 72° and the receding angle is 66° [7,54]. Chen et al. [55] compared the effect of hydrophilic (54°) and hydrophobic (104°) particles on the cavitation threshold. It is suggested that cavitation bubbles form more easily on hydrophobic particles. Compared to hydrophilic particles, the number of nuclei in water drastically increases.
in hydrophobic particle suspension. Belova et al. [56] reported that the TMAFM image of the sample in degassed water exhibited a simple two-phase liquid–solid interface without any nano- or micro-gas structures with longer AFM measurements (up to 60 min). However, Belova et al. [56] and Seddon et al. [57,58] observed the presence of sufficiently flat gas nanostructures with heights in the range of several nm and sizes of several μm that randomly formed on hydrophobized Si wafers in standard conditions (compared to degassed conditions). Those findings are consistent with the observations of Chen et al. [55].

As compared to bulk nanobubbles, it is important to note that there are relatively few studies on the effect of ultrasound parameters on surface nanobubbles. The discussion in Section 3 is mainly on the effect of ultrasound frequency on surface nanobubbles according to the AFM measurement results by Belova et al. [56] (20 kHz), Li et al. [48] (35 kHz), and Brotchie and Zhang [47] (515 kHz). In order to evaluate the influence of ultrasound pretreatment on surface nanobubbles, nanobubbles were produced on the surface of HOPG by the exchange of ethanol with water [54,59]. Belova et al. [56] reported that tapping mode atomic force microscopy (TMAFM) images after liquid exchange show the appearance of gas films on hydrophobic stripes (average height of 50–70 nm) with gas bubbles of different sizes and shapes sitting on top. Moreover, the hydrophilic areas were partially covered with
nanobubbles of a much smaller size (an average height is 30 nm and length is 100 nm), which remained stable for prolonged periods of time.

HOPG has a layered structure, with each layer being atomically smooth. HOPG commonly has a stable and reliable quality. In order to ensure the repeatability of tests, HOPG is widely used for the study of surface nanobubbles. Thus, the TMAFM images of nanobubbles on a HOPG surface taken prior to sonication and after sonication shown in Fig. 11 are considered to be accurate and repeatable. The lateral size distribution of surface nanobubbles on a HOPG was estimated using ImageJ software. The cumulative number fractions and differential number fractions as a function of the lateral size of nanobubbles were calculated according to the calculating procedures described in the literature [60,61]. Fig. 12 shows the effect of ultrasound treatment on the lateral size distribution of surface nanobubbles. Fig. 12 reveals that the number of nanobubbles smaller than 0.27 μm increased significantly after ultrasonication. Meanwhile, ultrasound treatment resulted in an increase in the number of nanobubbles larger than 6.2 μm. Furthermore, those nanobubbles with significantly smaller lateral sizes appeared in the vicinity of those newly generated, larger nanobubbles. It was concluded from Fig. 11 that the distribution of the lateral size of surface nanobubbles changed significantly after sonication for 30 s.

Brotchie and Zhang [47] displayed tapping mode AFM height images of nanobubbles prior to sonication and after sonication for 40 s. As shown in Fig. 13, it can be observed that the lateral size did not change appreciably in the presence of ultrasound. The Blake threshold defines the radius below which a bubble will oscillate in a smooth and stable manner and above which the bubble will undergo explosive growth and subsequent inertia collapse [62,63]. The calculated radii of curvature of nanobubbles (1.0–2.6 μm) observed on HOPG is very close to the radius of the Blake threshold (about 2.3 μm) in their experimental system. This theoretical analysis is in good agreement with the experimental results that the lateral size did not change appreciably when ultrasound irradiation was employed [47]. The intensity of bubble collapse (i.e., amount of energy released) and the maximum bubble size prior to collapse (resonance size) are correlated and approximately inversely proportional to the applied frequency [64]. The nuclei increase rapidly and then collapse within one period, which is known as transient cavitation [65]. As the ultrasonic frequency increases, the intensity of transient cavitation becomes weak. Instead, the stable cavitation effect is enhanced [66]. Unlike the collapse of cavitation bubbles at lower frequencies, bubbles produced at high frequency are much smaller and have a tendency to resonate rather than collapse [67]. The ultrasound frequency of 35 kHz employed in the study of Li et al. [48] is conducive to the occurrence of transient cavitation. According to the classical nucleation theory, it is difficult for the radius of gas nuclei to reach the bubble resonance radius of 35 kHz ultrasound frequency. As shown in Fig. 14, for 35 kHz ultrasound, the bubbles initially undergo growth and then collapse prior to reaching the bubble resonance radius of approximately 120 μm. Prior to reaching the bubble resonance radius, the bubble dynamic behavior of gas nuclei changed from growth to collapse (the occurrence of transient cavitation).

3. Proposed generation and stability mechanisms of nanobubbles in acoustic fields

3.1. Bulk nanobubbles

3.1.1. Generation mechanism

Bubble dynamics in the sound field can be divided into three types: oscillation, growth, and collapse [43]. When an ultrasonic wave contains a higher intensity than the “cavitation threshold,” tiny nuclei form internally, with their diverse behaviors in the opposite/negative pressure zone. The nuclei shrink or dilate, and if the nuclei dilate to a certain magnitude, then the gas molecules dissolved in the solution transfer into a nucleus to grow up to a nanobubble [28]. The bubble content, which is mostly water vapor, is widely observed at low ultrasonic frequencies with relatively high acoustic pressure amplitude. With higher ultrasonic frequencies, the cavitation bubble content is mostly non-condensable gas (such as air) [43]. It is well known that the low frequency (20–50 kHz) of ultrasound is beneficial for transient cavitation. After the collapse of the transient cavitation bubbles, the high impact results in transient cavitation effects, e.g., the mechanical effect, sonochemistry effect, and thermal effect. Unlike the collapse of cavitation bubbles at lower frequencies, bubbles produced at high frequencies around 1 MHz are much smaller and have a tendency to resonate rather than collapse [67]. Leighton et al. [68] proposed an equation to define the relationship between bubble resonance radius and ultrasonic frequency. The solution of this equation is shown in Fig. 14. For 35 kHz ultrasound, the bubble initially undergoes growth and then collapses prior to reaching the bubble resonance radius of approximately 120 μm. Prior to reaching the bubble resonance radius, the bubble dynamic behavior of gas nuclei has changed from growth to collapse (the occurrence of transient cavitation). The ultrasound frequencies of 20 and ~40 kHz of ultrasound probes are widely used for generating bulk nanobubbles [1,23-28,49]. Thus, the bubble dynamic behavior of gas nuclei has changed from growth to collapse (the occurrence of transient cavitation) prior to reaching the bubble resonance radius.

The concentration of dissolved oxygen in pure water drops significantly after the generation of nanobubbles [24,28]. It has been reported that the higher the oxygen concentration in water, the more nanobubbles are generated by ultrasound [24,28]. Jadhav and Barigou [23] developed a hypothesis that the collapse of microbubbles resulted from a 20 kHz probe-type processor, giving rise to the formation of bulk nanobubbles that previously went undetected. Mo et al. [28] proposed a
mechanism for bulk nanobubble generation by the ultrasonic method. The dissolved gases first enhance the formation of tiny bubbles during the ultrasonic process by receiving oscillation energy, which causes a lower concentration of dissolved oxygen. Then, with the ultrasonic time (from 0 to 10 min), small bubbles may start to coalesce into bigger ones, which decreases the concentration of the bulk nanobubbles. However, Nirmalkar et al. [24] found that an increase in ultrasonication time from 5 to 30 min led to a significant increase in the population of nanobubbles with moderate diameters (see Fig. 1), which indicates that the coalescence of nanobubbles occurs only with difficulty.

In classical cavitation theory, dissolved gas molecules act as nuclei for ultrasound cavitation. Kang et al. [69] demonstrated that an increase in the content of dissolved gases in water has been shown to improve acoustic cavitation intensity for the generation of microbubbles and their growth rate. Recently, Jin et al. [31] developed a pressure-driven method by repeating compression of the gas in aqueous solutions. According to the measurement results of virtue of optical microscopy and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, they speculated that the disappearance of microbubbles contributes to the formation of NBs, and the strong hydrogen bond at the gas–water interface prompts the stability of NBs. On this basis, the generation Mechanism of nanobubbles in an acoustic field can be attributed to the collapse of cavitation microbubbles. With the increase in the concentration of nuclei (i.e., dissolved gas molecules) or sonication time, the occurrence frequency of transient cavitation events (i.e., collapse of microbubbles) becomes higher, which therefore leads to an increase in the number of nanobubbles.

3.1.2. Stability mechanism

Cho et al. [26] showed that the effective diameter of nanobubbles in pure water is maintained at 750 nm without significant change within 1 h. Nirmalkar et al. [24] also reported that the mean diameter of bulk
nanobubbles remained stable after 350 days of storage. It was observed that these bulk nanobubbles generated by ultrasound are negatively charged and their zeta potential does not vary over time, which led some researchers to suggest that the constant surface charge on the bulk nanobubble surfaces is responsible for their stability [2,24]. In this mode, the stability of nanobubbles is supported by the electrically charged liquid–gas interface, which creates repulsion forces that prevent bubble coalescence, and by the high dissolved gas concentration in the water, which keeps a small concentration gradient between the interface and the bulk liquid [29,70]. Further, Yasue et al. [20,71] suggested a dynamic equilibrium model for a bulk nanobubbles partly covered with hydrophobic materials to explain the stability of bulk nanobubbles. This model has been suggested previously for surface nanobubbles [10], but it has been abandoned. In this model, the hydrophobic materials attached to the nanobubbles surface are suggested to provide a gas supply to stabilize nanobubbles. In addition, a stronger hydrogen bond was detected by ATR–FTIR spectroscopy during the shrinking of microbubbles into NBs [31]. Stronger hydrogen bonds are detected with a decrease in bubble size. Thus, it is presumed that the formation of a diffusion layer by adsorption of OH− is due to electrostatic interaction, contributing to negative surface charge, whereas the interaction of ions with the surface hydroxyl groups provides the equilibrium between the protonation and deprotonation of water and, finally, the formation of a stable interface layer [30].

Nirmalkar et al. [24] compared the bubble size distributions and bubble concentrations before freezing and after thawing of nanobubble suspensions generated in pure water. After freezing and thawing of the nanobubble suspensions, the bubble number density reduced to extremely low levels, approaching zero at low sonication times. No significant aggregation could have happened because the statistics of the size distribution before freezing and after thawing remained approximately the same. In addition, Tanaka et al. [17] observed that the indirect ultrasonic irradiation for 30 min reduced the number concentration of preexisting nanobubbles (prepared by pressurized dissolution method and swirling liquid flow method) by 90% regardless of the generation method. They also reported that the decrease in the bubble size under various sonication time indicates that the larger nanobubbles may have been destabilized first.

Yasuda et al. [1] investigated the effect of ultrasound frequency on the concentration of preexisting nanobubbles in pure water (prepared by the pressurized dissolution method). They found that the concentration of nanobubbles decreases with increasing ultrasound frequency. A simple model for the generation and reduction of nanobubbles by ultrasonic irradiation is proposed in Fig. 15. The bubble nuclei grow into cavitation bubbles with expansion and compression by way of nanobubbles. Cavitation bubbles mostly fragment into fine bubbles of various sizes, such as bubble nuclei and nanobubbles, due to collapse. The nanobubbles are generated due to the growth of bubble nuclei and the collapse of cavitation bubbles. The reduction in the concentration of nanobubbles is due to the growth of nanobubbles toward cavitation bubbles. Moreover, parts of nanobubbles and microbubbles aggregate by Bjerknes force and float to the water’s surface [1,66].

### 3.1.3. Surface nanobubbles

Belova et al. [56] found that preexisting surface nanobubbles on a solid-water interface lead to a significant increase (two times) in the number of pits on the hydrophobic areas after 10 min sonication time compared to the natural surface. The presence of pits is attributed to the collapse of cavitation bubbles [67]. This is considered to be due to the generation, expansion, growth, and collapse of nanobubbles induced by ultrasound irradiation. Cavitation bubbles can be shielded by neighboring ones that expand larger and collapse earlier. In this case, jetting flows produced by the collapsing bubbles have a horizontal direction, and no damage in the irradiated materials can be observed [72]. This finding is in good agreement with the presence of large surface bubbles shown in Fig. 11(b).

In addition, it has been confirmed that interfacial nanobubbles are stable and immobile and therefore should not be involved in the cavitation process [47,73]. However, we can observe that the height of surface nanobubbles increased markedly after being pretreated by 515 kHz ultrasound, whereas the lateral size did not change appreciably, indicating that the bubbles were pinned on the three-phase contact line. Thus, it is concluded that the pinning effect may play an important role in the stability of surface nanobubbles. However, Alheshibri et al. [2] systematically discussed the pinning mechanism of surface nanobubbles. They pointed out that the pinning mechanism implies that they should have the same radius of curvature, as they are necessarily in equilibrium with the same solution, when considering a population of neighboring nanobubbles on a surface. However, it can be observed from Fig. 11 and Fig. 13 that the lateral size distributions of surface nanobubbles are heterogeneous.

### 3.2. Prospects

#### 3.2.1. Effects of surfactant on bulk nanobubbles in acoustic field

Compared to pure water, Nirmalkar et al. [24] reported that the adsorption of sodium dodecyl sulfate (SDS) molecules on the nanobubble surface provides a “shielding effect” to nanobubbles against the effects of freezing and thawing. This mechanism is similar to the well-known phenomenon of steric/electro-steric stabilization of particle

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**Fig. 15.** Model for generation and reduction of nanobubbles by ultrasonic irradiation. According to Yasuda et al. [1] and Yasui [43].
suspensions [24,74]. Oeffinger and Wheatley [75] found that sonication time has no significant influence on the mean diameter of bubbles when solutions contain a mixture of surfactants (Span 60 and Tween 80). It is well known that the adsorption of surfactants on the bubble surface plays an important role in the generation and stability of bubbles. Thus, systematic studies on the effect of surfactant parameters (such as type, concentration, and synergistic mixture) on the generation and stability of nanobubbles in the presence of ultrasound should be performed.

3.2.2. Effect of the type of ultrasound equipment on nanobubbles at low frequencies

As discussed in Section 2.4, there is no systematic comparative study of the properties of bulk and surface nanobubbles between horn-type and bath-type ultrasound devices at low frequencies.

3.3. Effect of ultrasound parameters on surface nanobubbles

Applied ultrasound creates strong vibrations as well as stirring, and within the first few minutes, gas from the top of the reactor can be trapped in the liquid medium and contribute to bubble formation [56]. In addition, nuclei or tiny bubbles were reported to be trapped on rough and hydrophobic surfaces, which are typically nanoscale in size [2,45,76,77]. The presence of these very small bubbles has a profound effect on the interaction between particles and bubbles [78]. The presence of nuclei or nanobubbles on the solid-water interface is conducive to the occurrence of transient cavitation at low frequencies [26,56]. Chen et al. [46] found that flotation recovery of hydrophobic particles was reduced by more than 60% at 11 min following long-duration stirring or 20 kHz ultrasonic treatment compared to untreated micro-flotation tests (see Fig. 16). According to novel HIFU (high-intensity focused ultrasound) tests and cavitation threshold results [46,77], it has been demonstrated that bubbles trapped on the rough surface of hydrophobic particles are destroyed after long-duration stirring or ultrasonic treatment [46]. Some trapped bubbles will grow and then collapse. In addition, some trapped bubbles will continually expand, move to the liquid surface through buoyancy and radiation force, disappear at the liquid surface, and release gas into the atmosphere [43]. When hydrophobic particles are treated by stirring or ultrasonic devices, those trapped bubbles on particle surfaces are destroyed, and the flotation recovery hydrophobic particles are reduced significantly.

Brotchie and Zhang [47] observed that pretreatment with 515 kHz ultrasound can markedly increase the height of surface nanobubbles, which indicates that the gas diffusion phenomenon occurs. As discussed in Section 4.1, the ultrasound frequency is a significant factor for the determination of cavitation types. In addition to ultrasound frequency, ultrasound power and sonication time play an important role in determining bubble dynamics [43]. Therefore, the effect of the ultrasound parameters on surface nanobubble dynamics should be studied systematically.

3.4. Stability mechanisms of bulk and surface nanobubbles in an acoustic field

Some researchers have summarized and reviewed different stability theories or models of bulk and surface nanobubbles in recent years [2,5,6]. However, there is no effective research on the stability mechanisms of bulk and surface nanobubbles in an acoustic field.

3.5. The role of properties of substrates in the bubble dynamics of surface nanobubbles in acoustic fields

The degree of hydrophobicity and roughness have significant influences on the number of nuclei and the cavitation behaviors of the solid–liquid interface [55,56,79,80]. Belova et al. [56] evaluated the relationship between gas conditions and cavitation nucleation on planar solid surfaces with alternating hydrophobic/hydrophilic properties at 20 kHz ultrasound frequency. On this basis, further attention should be paid to discovering the effect of gas concentration (nuclei) on surface nanobubble dynamics at various ultrasonic frequencies and powers.

3.6. Role of the acoustic radiation force on dynamic behaviors of nanobubbles

Kobayashi et al. [81] explained the agglomeration behavior of microbubble swarms by the force balance between the Bjerknes force of the ultrasonic field and electrical repulsion of the microbubble surface. However, the role of the acoustic radiation force on nanobubble dynamics is still unclear.

4. Conclusions

In this paper, the effect of ultrasound parameters on bulk and surface nanobubbles was summarized. There are considerable contradictions in the experimental results from different studies, which can be attributed to the differences in the type of ultrasound equipment and the properties of the pure water, etc. There is no generally accepted theory of the generation and stability mechanisms of nanobubbles in acoustic fields. The transient and stable cavitation theory could be a promising tool to reveal the generation of nanobubbles by ultrasound. The synergistic effect of the electrical double-layer interaction force and hydrogen bond plays an important role in the stability of bulk nanobubbles. The hydrophobicity and morphological characteristics have a significant effect on the interaction between particles and bubbles [78]. The presence of nuclei or nanobubbles on the solid-water interface is conducive to the occurrence of transient cavitation at low frequencies [26,56]. Chen et al. [46] found that flotation recovery of hydrophobic particles was reduced by more than 60% at 11 min following long-duration stirring or 20 kHz ultrasonic treatment compared to untreated micro-flotation tests (see Fig. 16). According to novel HIFU (high-intensity focused ultrasound) tests and cavitation threshold results [46,77], it has been demonstrated that bubbles trapped on the rough surface of hydrophobic particles are destroyed after long-duration stirring or ultrasonic treatment [46]. Some trapped bubbles will grow and then collapse. In addition, some trapped bubbles will continually expand, move to the liquid surface through buoyancy and radiation force, disappear at the liquid surface, and release gas into the atmosphere [43]. When hydrophobic particles are treated by stirring or ultrasonic devices, those trapped bubbles on particle surfaces are destroyed, and the flotation recovery hydrophobic particles are reduced significantly.

Brotchie and Zhang [47] observed that pretreatment with 515 kHz ultrasound can markedly increase the height of surface nanobubbles, which indicates that the gas diffusion phenomenon occurs. As discussed in Section 4.1, the ultrasound frequency is a significant factor for the determination of cavitation types. In addition to ultrasound frequency, ultrasound power and sonication time play an important role in determining bubble dynamics [43]. Therefore, the effect of the ultrasound parameters on surface nanobubble dynamics should be studied systematically.

3.4. Stability mechanisms of bulk and surface nanobubbles in an acoustic field

Some researchers have summarized and reviewed different stability theories or models of bulk and surface nanobubbles in recent years [2,5,6]. However, there is no effective research on the stability mechanisms of bulk and surface nanobubbles in an acoustic field.

3.5. The role of properties of substrates in the bubble dynamics of surface nanobubbles in acoustic fields

The degree of hydrophobicity and roughness have significant influences on the number of nuclei and the cavitation behaviors of the solid–liquid interface [55,56,79,80]. Belova et al. [56] evaluated the relationship between gas conditions and cavitation nucleation on planar solid surfaces with alternating hydrophobic/hydrophilic properties at 20 kHz ultrasound frequency. On this basis, further attention should be paid to discovering the effect of gas concentration (nuclei) on surface nanobubble dynamics at various ultrasonic frequencies and powers.

3.6. Role of the acoustic radiation force on dynamic behaviors of nanobubbles

Kobayashi et al. [81] explained the agglomeration behavior of microbubble swarms by the force balance between the Bjerknes force of the ultrasonic field and electrical repulsion of the microbubble surface. However, the role of the acoustic radiation force on nanobubble dynamics is still unclear.

4. Conclusions

In this paper, the effect of ultrasound parameters on bulk and surface nanobubbles was summarized. There are considerable contradictions in the experimental results from different studies, which can be attributed to the differences in the type of ultrasound equipment and the properties of the pure water, etc. There is no generally accepted theory of the generation and stability mechanisms of nanobubbles in acoustic fields. The transient and stable cavitation theory could be a promising tool to reveal the generation of nanobubbles by ultrasound. The synergistic effect of the electrical double-layer interaction force and hydrogen bond plays an important role in the stability of bulk nanobubbles. The hydrophobicity and morphological characteristics have a significant

![Fig. 16. Micro-flotation results for molybdenite with different stirring times (a) and ultrasonic treatment times (b). No stirring (or ultrasonic) indicates that the sample was dried after 2 h of stirring (or ultrasonic). The line was obtained by fitting the classical first-order model of flotation kinetics to experimental data of the micro-flotation results. The original data were collected from the literature [46].](image-url)
influence on acoustic cavitation, which has an important influence on nanobubble dynamics. It is expected that a combination of the conventional stability theories of surface nanobubbles and the acoustic cavitation theory will help us to better understand the stability of surface nanobubbles in acoustic fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary data

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