
Current status of research on nanobubbles in particle flotation

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Abstract: Froth flotation, as one of the most widely used separation approaches in mineral processing, is commonly used to recover valuable components from minerals. However, maintaining high flotation efficiencies is a serious challenge for conventional froth flotation in the face of decreasing particle size of the minerals to be sorted. To date, there have been plenty of reports on the software of nano-bubbles (NBS) in flotation, and the experimental consequences show that nano-bubbles' introduction has given rise to improvement's different grades in the recovery of varieties of minerals, which highlights the great potential of nano-bubbles for mineral flotation. Nanobubbles have smaller bubble radii and unusually high stability compared to conventional flotation bubbles, and their related behavior in flotation has been a hot research topic. This paper reviews some of the methods of preparing nanobubbles, equipment techniques for characterizing nanobubbles, factors affecting their stability, and some of the popular doctrines. In particular, the reinforcing mechanism of nanobubbles in the particle flotation process is discussed, first, the nanobubbles improve the electrostatic attractiveness with the particles by achieving the charge inversion while the nanobubbles that was adsorbed on the particles' surface will cover a share of the charge, which decreases the electrostatic repulsive force between the particles; and second, the nanobubbles can act as a bridge between the surfaces of the two particles, which advances the agglomeration between the particles. This review aims to be able to further advance the research related to the industrialization of nanobubbles.

Keywords: nanobubbles, particle flotation, collision probability, stability, aggregation

1. Introduction

Froth flotation is used for serviceable minerals' separation commonly in mineral processing. Before froth flotation is carried out, the minerals need to be crushed and screened in advance to achieve a suitable particle size. Currently, in the context of diminishing mineral resources, minerals are becoming smaller and smaller under the action of the grinding system in order to achieve the requirements for full extraction, which leads to a decrease in the efficiency of sorting. Therefore, the realization of efficient froth flotation recovery of both conventional mineral particles and fine-grained grades remains a long-term challenge for the mineral processing industry.

In order to improve the enrichment ratio of target minerals in froth flotation, researchers have used optimization of flotation circuit control (Wepener et al., 2023) and the use of hybrid collectors (Farid et al., 2022), and the flotation recoveries have been improved to different degrees in the experimental results. As stated by some recent reports, the application of nanobubbles in froth flotation, however, has also reached nice results (Sobhy et al., 2021; Wang et al., 2022).

Nanobubbles (NBS), referring to bubbles <1 μ m in diameter (Oliveira et al., 2018), were firstly hypothesized to exist in 1994 by Parker et al. (1994) to excuse the attractive forces existing between two hydrophobic surfaces. Due to the active performance of NBS in the treatment of organic wastewater (Calgaroto et al., 2016; Wu et al., 2021; Levitsky et al., 2022), mitigation of surface corrosion (Kioka and Nakagawa, 2021), food processing (Thi Phan et al., 2020), etc., which highlights its wide range of applications, it has invited plenty of attention. In the mineral flotation industry, +according to recent studies (Liu et al., 2021; Zhang et al., 2021c), NBS's introduction in the flotation process can realize the improvement of mineral recovery and flotation rate.

In order to reveal NBS's promotion effect in mineral flotation, according to a series of research work by researchers, the more recognized viewpoint is that NBS can not only promote the adsorption and collision between macro bubbles and particles, but also prevent flotation chemicals' further adsorption on the particles' surface, and enhance the hydrophobicity of the particles at the same time its own can reduce the dosage of trapping agent and foaming agent, which reduces the consumption of flotation chemicals (FAN et al., 2010a; Sobhy and Tao, 2013b; Nazari et al., 2022). Moreover, NBS was also found to have excellent performance in recovering fine particles, the mechanism of which will be discussed in the following section. An in-depth sympathy of the role of the role of NBS in granular flotation is important for the development of more efficient and improved technologies for granular flotation.

In practice, the froth flotation process is in a complex solid-liquid-gas three-phase environment. Due to the distinctions in the properties of NBS in comparison with traditional foams, the introduction or replacement of NBS with conventional foams in froth flotation is a new area of research. In this paper, some of the research progress of the work carried out on NBS in recent years is reviewed, including the observation techniques, stability, and enhancement mechanisms in particle flotation and some of the results in fine particle recovery, with the aim of providing some cursory information for further work on the development of NBS for conventional/fine particle recovery technology.

2. Current status of NBS research

2.1. Preparation and properties of NBS

With the deepening of NBS-related research, different means of preparing NBS have been developed, such as ultrasound (Chen et al., 2021), hydrocavitation (Li et al., 2022c; Ma and Tao, 2022; Zhou et al., 2022b), pressurization in water (Etchepare et al., 2017b), generation in microfluidics (Labarre et al., 2022), etc., which are commonly used to prepare NBS on a small scale in the laboratory. However, in real industrial flotation, in order to make NBS fully effective in flotation cells, batch generation of NBS is required. However, in real industrial flotation, if NBS is to be fully utilized in the flotation cell, it needs to be generated in large quantities, and the most commonly used method for preparing NBS in large quantities is hydrocavitation (HC). Hydrocavitation's principle is to produce bubbles by diminishing the pressure to a certain critical value through a change in the flow rate of the flowing liquid causing a change in the pressure of the system. Hydrocavitation is popularly used in industrial flotation for NBS flotation systems because it is easy to control in industry by adjusting geometric conditions, velocity and other parameters, and it is easy to operate, and different sizes of NBS can be generated by containing the liquid flow rate (Oliveira et al., 2018; Han et al., 2020). In 2010, FAN et al. (2010a) used hydrocavitation to prepare NBS in a homemade NBS generation system to study its effect on froth flotation and found that dissolved oxygen and carbon dioxide gases in water enhanced the NBS generation process. It has been reported in the literature that saturated air in water after depressurization can also prepare very stable NBS (Calgaroto et al., 2014; Azevedo et al., 2016).

However, the preparation of NBS by hydrocavitation not only needs to consider the role of gas on bubble formation, but also needs to consider the influence of other factors. Zhou et al. (2022b) investigated the impact of preparation time and aeration rate of hydrocavitation on bulk NBS's aqueous properties, and the results indicated that with the prolongation of the preparation time and the increase of the aeration rate, the concentration of NBS firstly increased and then decreased, and the diameter firstly decreased and then increased. Agarwal et al. (2022) investigated whether the salting out effect contributes to the nucleation of NBS and confirmed by refractive index calculations that an increase in the salt content in water leads to a decrease in the solubility of gases in water, which results in the presence of excess dissolved gases in the form of NBS, and Olszok et al. (2020) carried out comparative experiments by pressurizing particles with different properties in water, respectively. The consequences demonstrated that the surface properties of the particles play an important part in NBS's generation and that the surface formation of NBS has a dependence on the hydrophobicity and surface roughness of the particles. Mikhlin et al. (2020) applied AFM to picture the surface of galena preheated and then treated with cold water and reported that metal sulfides will promote the formation of NBS after initial contact with cold water after high temperature treatment. As the temperature increases, this approach, known as pyrolysis, is based on the principle the solubility of gases in solution diminishes, leading to supersaturation of the gases and the release of excess gases at the surface through the formation of gas

bubbles. Because a gas' solubility is fixed by temperature, gas type, liquid pressure, and other factors, a certain liquid temperature the same prefers NBS's structure.

Another popular method of preparing NBS is the solution exchange method. This method is based on the fact that gases in two liquids with different solubility will be separated due to the mixing between the liquids, and the overflow gas will be preserved in the form of bubbles. In order to better understand formation mechanism of NBS over the solvent exchange process, Xiao et al. (2017) used MD simulation to study the kinetic properties of NBS after solvent exchange, and discovered that in solvent exchange's early stage, there exists an interface between solvents with distinct gas solubilities, which will bit by bit move toward the substrate that was driven by the gas concentration gradient, and make the gas molecules move toward the interface in the process of supersaturation phenomenon, which promotes the NBS formation. Zhang et al. (2006,2007) found that no NBS appeared on the silicon surface immersed in water/saturated CO₂, and the presence of NBS was found after solution exchange, which explains that the gas inside the NBS originates from the dissolved gases in the solution. Among the solution exchanges the ethanol-water combination has been widely used (Hampton and Nguyen, 2009; Ding et al., 2020), probably because it does not introduce other impurities during the operation that can cause interference in the identification of the observation equipment (Lou et al., 2000). However, it should be noted that the complexity of the liquid environment during solvent exchange makes it difficult to control the liquid parameters (e.g., gas saturation) in a stable manner, thus making it difficult to achieve stable generation of bubbles by this method.

2.2. Observation techniques for NBS

In the past, under conditions where observation techniques were not yet developed, there were difficulties in distinguishing NBS from other nanoscale substances because of the very small size of NBS. Due to the lack of differentiation ability of observation equipment, there have been cases where staff have incorrectly identified nanodroplets or nanoparticles as NBS. Therefore, the use of accurate detection means is particularly important for NBS-related research. At present, with the in-depth study of NBS, various measurement techniques have been introduced, among which the commonly used methods are: AFM, DLS, NTA, etc. The size distribution of NBS is not only the same as that of nanodroplets, but also the size distribution of nanoparticles. It is worth mentioning that the size and distribution of NBS depend greatly on the system design and operating conditions in the experimentations (Lou et al., 2000), so the accurate characterization of NBS in different experimental environments is the key to the relevant exploration of its properties and the assessment of its potential. This section describes a portion of the NBS observation techniques.

2.2.1. Atomic Force Microscopy (AFM)

The AFM was first developed by Binnig and coworkers in 1986 (Binnig et al., 1986). The device is capable of imaging the surface topography of the sample to be tested with nanometer-scale resolution and is able to measure the interaction forces between other surface systems by the sample and the tip (Fig. 1 e).

The principle of AFM is to perform raster scanning on the surface of the sample to be gauged with the help of a tip probe, during which the degree of the cantilever's deflection is controlled by means of a position-sensitive diode detector (PSD) and a three-dimensional morphology image is obtained under the set conditions. Based on Hooke's law, the degree of deflection of the cantilever is converted to calculate the value of the interaction force with a measurement accuracy of pN. AFM has become one of the most popular techniques to study the properties associated with NBS.

Surface NBS were first imaged using the tap mode of AFM as early as 2000 by Ishida et al. (2000) and Lou et al. (2000), Lou found that the size of NBS on highly oriented pyrolytic graphite (HOPG) (Fig. 2a) was larger than that on mica surfaces (Fig. 2b) and could be maintained for several hours without disappearing.

In a recent study, Owens et al. (2019) used non-contact atomic force microscopy (NC-AFM) to image surface NBS on a lustrous cross-section taking rare earth minerals and indicated that the use of NBS to determine hydrophobicity is particularly applicable to highly complex ores with small particle sizes. Ren et al. (2023) found that NBS not only reduces the amount of trapping agent used during flotation,

but also improves the flotation and recovery of fine-grained cassiterite, and AFM showed results indicating that NBS can suppress the adsorption of caprylohydroxamic acid (CHA) on the mineral surface. Zhang et al. (2021b) analyzed that NBS can be produced on hydrophobic surfaces at temperatures ranging from 5 ± 1 °C to room temperature of 25 °C based on AFM measurements. Li et al. (2020a) questioned the effect of using ultrasound to produce NBS on the graphite particles settling efficiency and the flotation performance as no NBS was found at the HOPG-water interface by AFM under ultrasonic treatment, which could be due to flotation system differences resulted. Zhou et al. (2020b) used AFM to observe the change of bubbles on the surface of dolomite with increasing temperature, and the observations showed that NBS can undergo stable nucleation on the surface of fine-grained dolomite when the temperature of the slurry rises during the process. Wang et al. (2019b) based on the imaging results of AFM and further experimental results reported that the coverage area of sodium oleate on the calcite surface decreased by about 30% under reduced pressure conditions compared to constant pressure, and by about 20% at pH=10, due to the fact that NBS occupies the

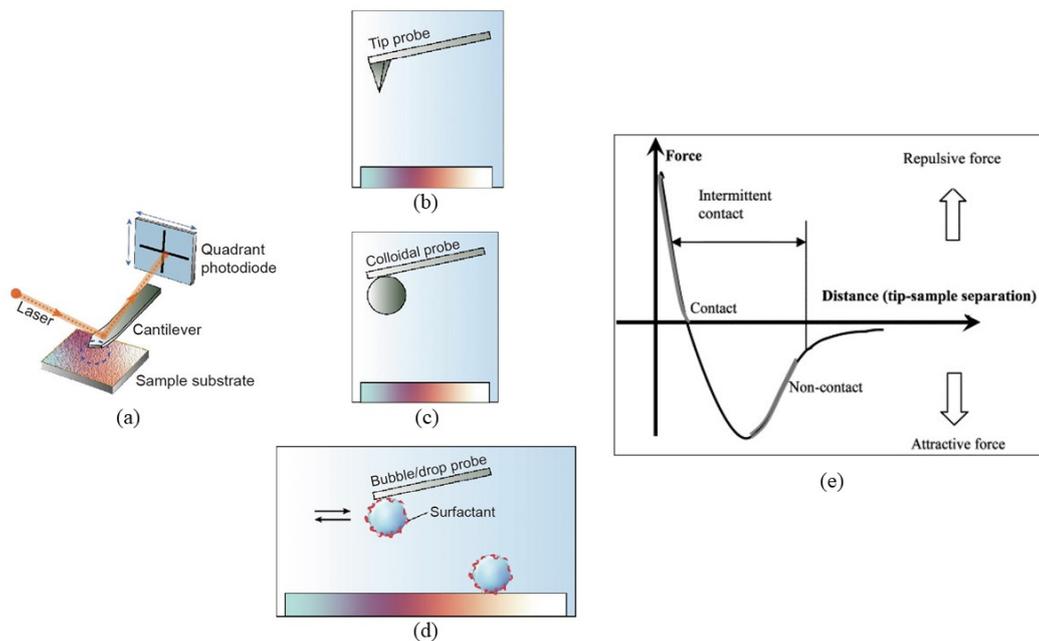


Fig. 1. (a) Principle of AFM observation, and (b)-(d) different probe types: (b) nanoprobe, (c) colloidal probe, (d) bubble probe (Zhang and Zeng, 2021). (e) Curve of atomic force magnitude as a function of the distance between the AFM tip and the sample to be measured (Jalili and Laxminarayana, 2004)

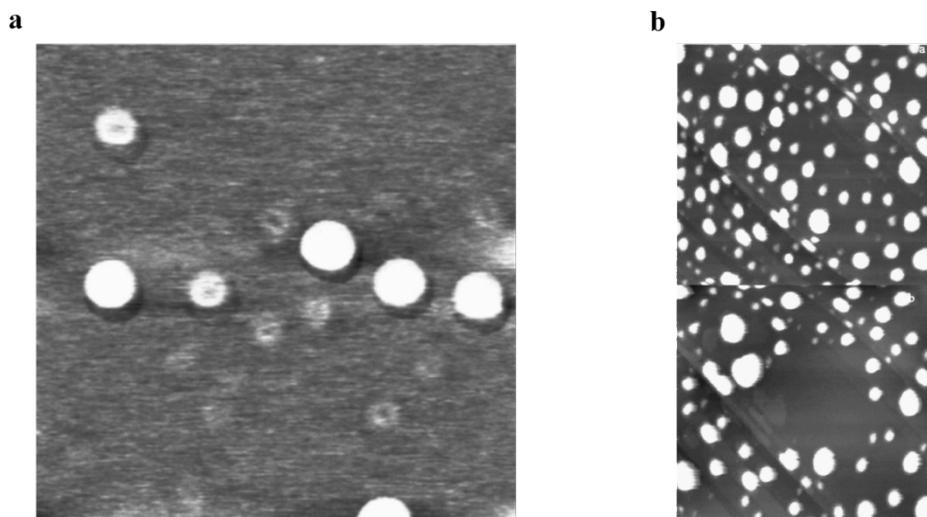


Fig. 2. AFM image of surface bubbles of mica (a) and HOPG (b) in water observed in tapping mode (Lou et al., 2000)

surface of the minerals to cause a bridging effect and inhibit the adsorption of surfactants, and this report supports the idea that NBS can reduce the amount of the agent used.

In addition to obtaining conventional imaging information, the ability to measure different interaction forces in selected systems by modifying the tip of an AFM extends the application of AFM for nanoscale observations. Currently, the assembly of individual long-chain polymers by the tip (i.e., single-molecule force microscopy) (Xie et al., 2019), the assembly of colloids to form colloidal probes to measure the attraction forces between hydrophobic surfaces (Fig. 1b) (Azadi et al., 2020), and the immobilization of gas bubbles on hydrophobized cantilever beams to form gas bubble probes (Cui et al., 2016) (Fig. 1d) have emerged, among others. Moreover, it is possible to differentiate NBS from nanoparticles/nanodroplets that is based on distinct force curve models calculated by AFM, and data such as NBS's contact angle is calculable from the resulting image. A hydrophilic tip is used if the geometric size of the NBS needs to be obtained. The use of tip probes inevitably causes interference with the observed samples, however, it has been reported that the formation of NBS does not correlate with the use of probes (Lohse and Zhang, 2015).

2.2.2. Dynamic Light Scattering (DLS)

DLS can be used to gauge the distribution of bubble sizes and particle in a solution. The principle of measurement is based on the particles in solution continue to do irregular Brownian motion, resulting in changes in the intensity of scattered light irradiated particles (Fig. 3) , and then use the intensity of the photon correlation function to analyze the movement of the particles, the calculation of the particle's translational diffusion coefficient D , and converted according to equation (1) to get the particle radius R .

$$D = \frac{k_B T}{6\pi\eta R} \quad (1)$$

where, k_B is the Boltzmann's constant, T is the temperature and η is the dynamic viscosity of the solution.

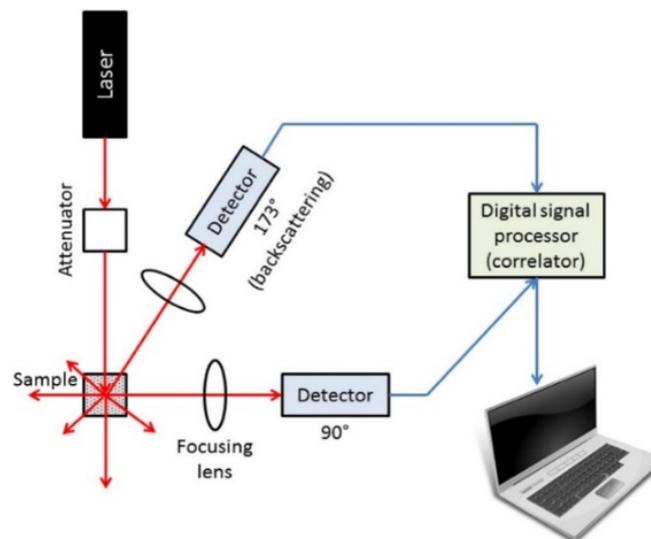


Fig. 3. DLS generally consists of a laser, a sample to be measured, and a photodetector (Bhattacharjee, 2016)

The measurement size range of DLS is generally within 5-10,000 nm, which makes it suitable for the characterization of nanoscale NBS. It should be noted, however, that because of the dynamic motion of the small bubbles, the results of a single measurement are generally subject to error, and therefore multiple measurements of the sample are required in the experiment. Also DLS only provides relevant dimensional data and is unable to measure bubble number density (Nirmalkar et al., 2018b), as well as not having the ability to provide chemical information itself that can be used to differentiate between NBS and particles/droplets (Jin et al., 2020). The Brownian motion of NBS in a multivariate system may be affected to some extent by the presence of other particles, leading to fluctuations in the DLS measurements. Zhang et al. (2020a), in studying the role of NBS in promoting the formation of virus-

like particles (VLP, around 26 nm), concluded that the self-assembly of CPs (viral capsid proteins) was due to NBS-driven, and found that the particle radius of the VLP as derived by DLS was highly similar to that measured by AFM, with all the detected radii of the particles being centered at 27 nm. This may be due to the environment being a binary system, the small size and low concentration of CPs have a weak effect on NBS movement, resulting in unaffected detection by DLS. Panchal et al. (2014) claimed that DLS is unable to discriminate between particles in binary mixtures that differ in size by a factor of less than ten. Therefore, if DLS is to be used for NBS measurements, it is important to know whether the environment in which the NBS is located is suitable for this technique, as DLS is easy to use, has a short measurement time, and can accurately measure the particle size, but it can be easily affected by the environment in which it is to be measured as well as by other particles. For polydispersed solutions other means of observation, such as nanoparticle tracer analysis, should be considered.

2.2.3. Nanoparticle tracer analysis (NTA)

In the same way as DLS, NTA works on the same principle based on the scattering of light. This method is an observational tool for tracking and analyzing individual particles in liquids, which can be displayed in real time (Etchepare et al., 2017a), and at the same time, the particles' flow dynamics are calculable based on the Brownian motion of the analyzed particles, which compensates for the trouble of distinguishing between NBS and nanoparticles observations by the DLS technique. It has been reported that NTA can also yield particle size and concentration of particles (Batchelor et al., 2021). Since the technique can distinguish between different types of particles/substances of similar sizes, NTA can be applied to the characterization and detection of NBS in multivariate systems. NTA can be used to calculate the particle size from equation (2) based on the rms displacement of the particles collected by light irradiation (Fig. 4).

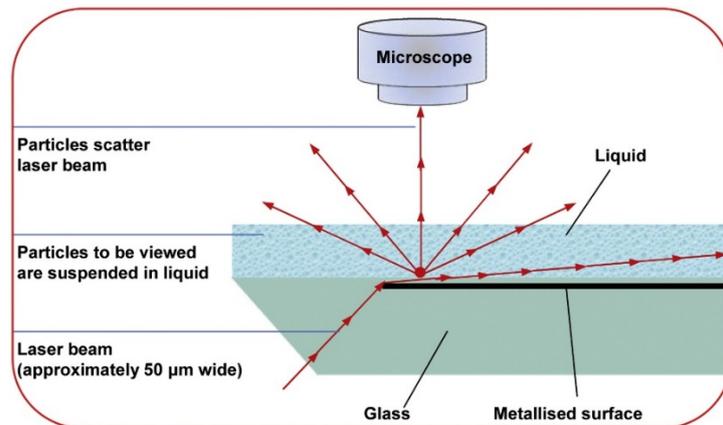


Fig. 4. NTA utilizes microscope objective detection to track the movement of individual particles based on the scattered light from the sample (Dragovic et al., 2011)

$$\langle x,y \rangle^2 = 4tD \quad (2)$$

where $\langle x,y \rangle^2$ is the 2D displacement measured at moment t , D is the particle translational diffusion coefficient.

According to the measuring range of NTA (10-1000nm), basically different sizes of NBS can be observed, and the diameter of NBS can be accurately calculated by combining the ultramicroscope with the light irradiation unit. Compared to DLS, NTA is able to obtain a more detailed bubble size distribution. However, according to some researchers, the technique is unable to observe larger NBS (Batchelor et al., 2021). In the study of Abenojar et al. (2020) using NTA was unable to detect particles with ruler diameter > 400 nm, which led to errors in the observations. Moreover, due to the randomness of the particles undergoing Brownian motion, the calculation results of NTA are still somewhat statistical. Irregular operation (e.g., the use of inhomogeneous illumination and different intensities of scattered light can prevent the instrument from doing accurate discrimination due to irregular displacement of particles near the focal point (Block et al., 2016)) can also contribute to the error in the

observation results. The ability of NTA itself to measure accurately is highly dependent on the setup in which the data are collected and analyzed (Gross et al., 2016). Several researchers have now classified the application of this technique to NBS analysis as a suitable method (Rosa and Rubio, 2018; Yasuda et al., 2019; Olszok et al., 2020).

2.3. Stability of NBS

The stability of bubbles generally refers to the length of the lifespan of the bubbles' existence. According to past experimental reports, NBS possesses a long lifetime (Ward et al., 1983), which can last for days or weeks (Zhang et al., 2008; Ushikubo et al., 2010; Azevedo et al., 2016; Etchepare et al., 2017b). And as the stability increases, the average size of NBS increases (Bu et al., 2022). Curiously, the high stability that NBS possesses compared to the highly fragile nature of conventional flotation foams is quite bizarre and creates a discrepancy between this property and what has been previously modeled for foams.

The E-P model proposed earlier by P. S. Epstein and M. S. Plesset (Epstein and Plesset, 1950):

$$\epsilon \approx \left[\gamma + (1 + \gamma^2)^{\frac{1}{2}} \right] x, \quad \epsilon, x \gg 1 \quad (3)$$

Young-Laplace model:

$$\Delta P = \frac{2\gamma}{r} \quad (4)$$

where ϵ is the ratio of bubble radius to initial radius, γ is the surface tension, x is the bubble radius length, ΔP is the pressure difference between inside and outside the bubble, r is the radius of a bubble.

NBS, as nanoscale spherical bubbles, has a very small gas volume and radius. The E-P model (3) predicts that diffusion or dissolution of NBS should occur within milliseconds to microseconds. According to Eq. (4) NBS is subjected to high gas pressure by generating Laplace force inside, and such bubbles are instantly dissolved under high pressure, which makes NBS an unstable gas system from the thermodynamic point of view. Both models predict that bubbles will become very fragile due to the shrinking radius of the bubble. However, in fact NBS is very good at this stability, which is inconsistent with the results predicted by the two models mentioned above. Ma et al. (2021) suggested that this phenomenon can be understood as a competition between simultaneous inflow and outflow of gas inside the bubble. With further studies, it was shown that NBS's stability is not only connected to the gas supersaturation and surface hydrophobicity (Tan et al., 2018), but also to the chemical properties of the agent (Nazari and Hassanzadeh, 2020).

In order to maximize the utilization of NBS in the flotation process, the stable existence of NBS is particularly important. In the actual flotation system, in order to enhance the stability of NBS, the more direct method is to regulate the physical parameters of the solution, thus causing changes in the properties of NBS. It can be considered from the two major aspects of the solution pH and temperature.

2.3.1. Effect of pH on the stability of NBS

It is well known that NBS can maintain a long lifetime in alkaline medium, the principle is that OH⁻ on the surface of bubbles affects the surface charge accumulation of NBS, and the solution under strong alkaline conditions can provide sufficient OH⁻ wrapped around the surface of NBS to stabilize the double electric layer. Therefore, some scholars believe that NBS is unstable under acidic conditions, which is because H⁺ cannot replace OH⁻ to play the role of stabilizing the double electric layer (Nirmalkar et al., 2018a), and NBS will dissipate after one or two days (Ferraro et al., 2020).

It is known that in suspension systems if the particles all exhibit high zeta potentials, they remain relatively stable over a longer period of time and are less prone to aggregation and merging (Gurung et al., 2016), which reflects a physical property of particles. And NBS exhibits similar characteristics to particles in this respect. NBS first adsorbs OH⁻ from the solution to form a surface negatively charged ionic layer, which is followed by electrostatic attraction of charged H₃O⁺ ions to form a bilayer (Fig. 5).

Fig. 5 explains that the closely spaced hydroxyl ions on the surface of the stabilized NBS inhibit the outward diffusion of gases within the bubbles, and the repulsive force between the hydroxyl ions can be used to balance the surface tension of the NBS to preserve the NBS's stability. This is one of the reasons why NBS maintains high stability in alkaline environments, because sufficient amounts of OH⁻ can maintain the double layer structure of NBS, and this effect also makes it possible to prevent bubble

agglomeration by electrostatic repulsion between NBSs, and neighboring NBSs do not come into contact easily with each other. The presence of electrostatic repulsion increases the resistance to bubble agglomeration and thus NBS exhibits high stability (Calgaroto et al., 2014). This has arrived at the belief that NBS is more balanced in alkaline environments than in acidic environments, which is still widely held today, and is supported by theory and relevant experimental data. From Fig. 6, it can be seen that the average size of NBS rises with decreasing pH, while the bubble number density decreases. This may be due to diffusion of some of the NBS during the decrease in pH.

Zhang et al. (2020b) found that OH⁻ encapsulated on the surface of NBS will be affected by the competing adsorption of bubble molecules in solution, a result that helps to further understand the stability of NBS in different environments.

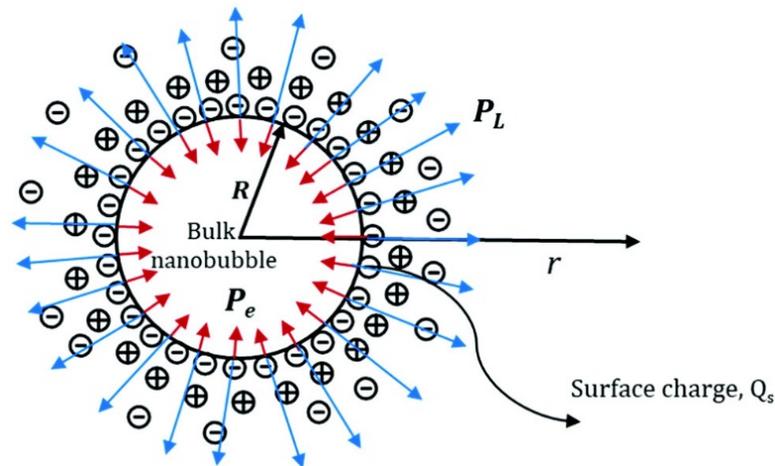


Fig. 5. Schematic diagram of the Laplace pressure inside the NBS and the external electrostatic pressure balancing each other when negative charges are wrapped around the NBS surface (Nirmalkar et al., 2018a)

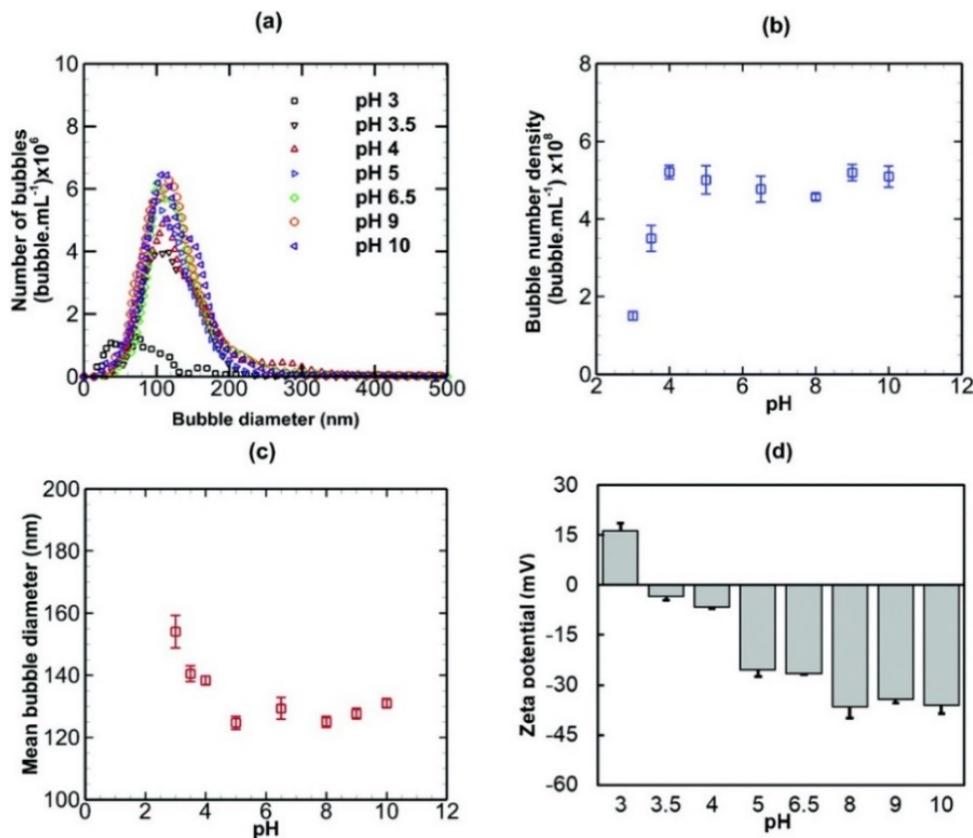


Fig. 6.(a)-(d) correspond to the bubble size distribution (a), bubble number density (b), mean bubble diameter (c), and the variation of suspension zeta potential (d), respectively, for pH vs. NBS (Nirmalkar et al., 2018a)

However, recent studies have reported that NBS can remain relatively stable under excessively acidic conditions and that the number of bubbles does not decrease with decreasing pH. Ma et al. (2022b) carried a study out on NBS's evolution in acidic media. By varying the sonication time, three different number concentrations of nanobubble suspensions were generated in aqueous solutions of pH = 3, pH \approx 5, and pH = 9. Extraction and characterization at different time intervals revealed that the stability of NBS was better in pH = 3 and pH = 9 solutions, but the number of NBS disappeared by about 60% to 80% within 24 h in pH = 5 solution (Fig. 7). This suggests that NBS's stability is linked to the surface charge/attached ions strongly. A large number of cations/anions can be wrapped around the NBS surface to keep it stable, and it is the net charge's absolute value on the NBS surface considered here, regardless of positive or negative.

In the experiments of Zhang et al. (2023) it was observed that NBS in both environments under acidic and alkaline conditions were smaller in size and more stable as compared to neutral conditions, showing that pH plays a role in maintaining the stability of the NBS, which may be due to the effect of the accumulation of the surface charge of the NBS by the NaOH and HCl used, besides the further findings showing an rise in the NBS's concentration with surfactants' addition, which may be associated with the surface tension of the solution. According to the studies carried out by Fu et al. (2021) and others on NBS in biological denitrification, it was found that when the absolute value of the zeta potential of NBS increased, the number of NBS showed an overall increasing trend. Thus, whether the solution pH is too low or too high, positive/negative ions can encapsulate the NBS surface, thus increasing the absolute value of the NBS's zeta potential, and reducing bubble aggregation through the enhancement of electrostatic repulsive force while this high potential structure will maintain the NBS stability (Fig. 8).

It is hypothesized that the reason for the difference in the results of the previous experiments may be due to the matching relationship between the pH of the medium and the IEP value of NBS, or it may be due to the difference in the nature of NBS caused by the different production processes used to prepare NBS. In general, however, NBS can also be stabilized under peracidic conditions under certain conditions. In the past, this may have been because experimental results generally showed a preponderance of NBS observed in high pH environments. When Zhang et al. (2006) added acidic solutions H₂SO₄ and HCl, as well as alkaline solutions KOH and NaOH, respectively, to NBS solutions produced by ethanol-water exchange, they found that there was no measurable change in the scale of

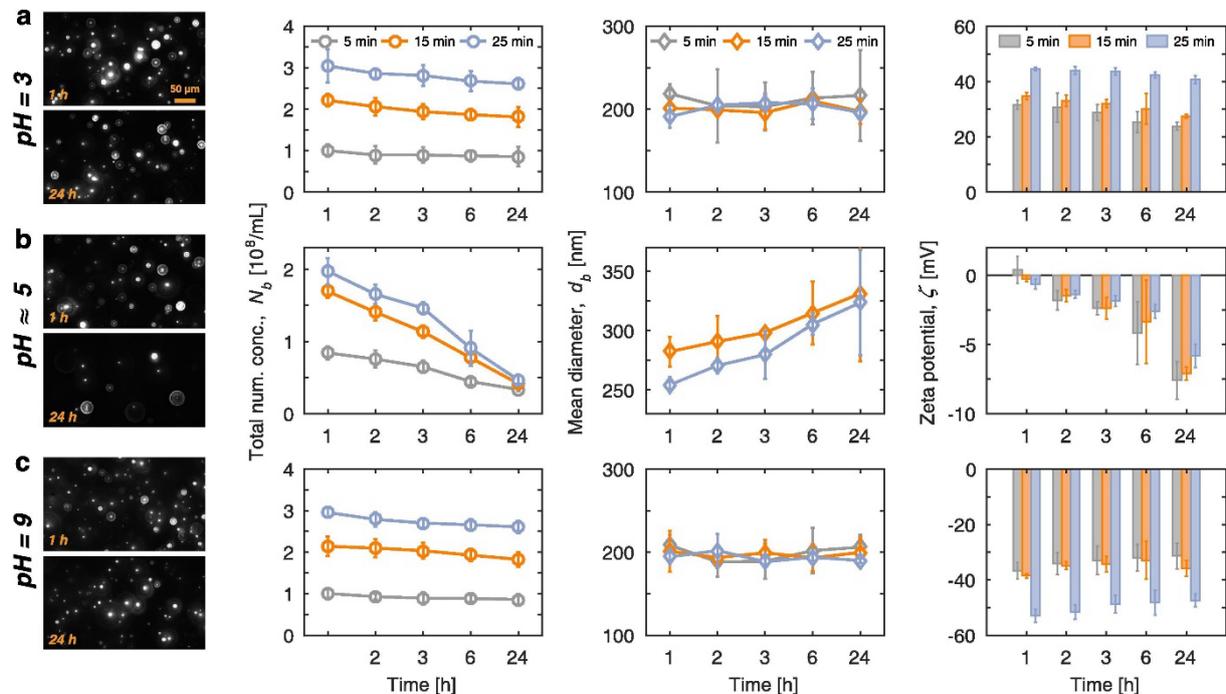


Fig. 7. Evolution of the number of NBS, average diameter and ζ -potential over time in three solutions at pH=3 (a), pH \approx 5 (b), and pH=9 (c) for sonication times of 5, 15, and 25 minutes, respectively. On the far left are images of light-centered scattering in the presence of ultrasound at 1 and 24 h after NBS formation (Ma et al., 2022b)

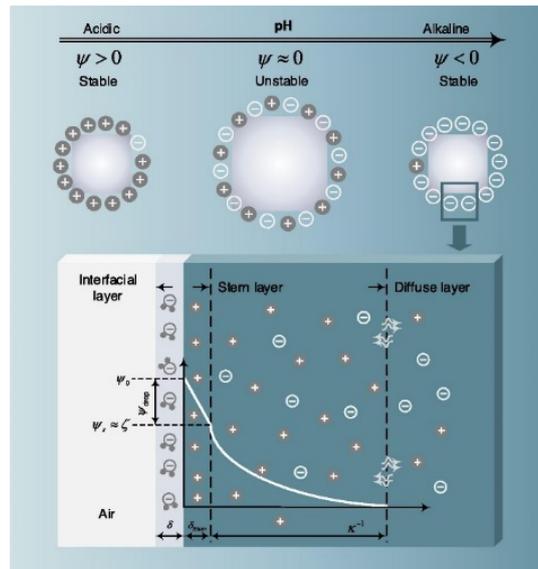


Fig. 8. Stabilization of NBS in excessively acidic or alkaline environments and schematic representation of the double electric layer constructed by negative charges on the surface of NBS (Ma et al., 2022b)

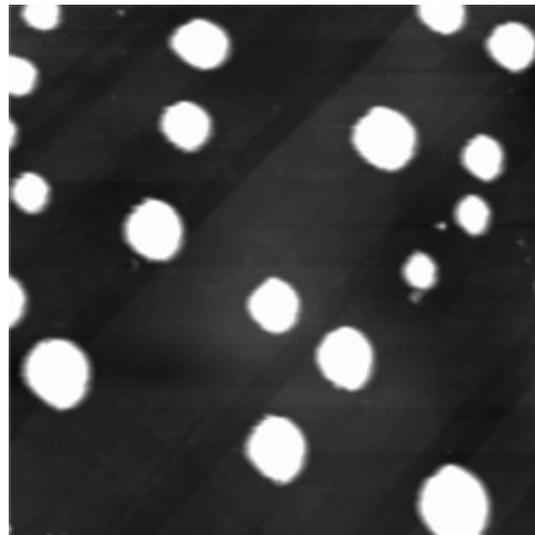


Fig. 9. NBS on the surface of HOPG in a concentration of 0.5 M NaCl. After ethanol-water exchange to form NBS, the NBS did not disappear when 0.5 M NaCl solution was substituted for water. Using acid and base solutions in place of water, the NBS was similar to that of the previous (Zhang et al., 2006)

the NBS (Fig. 9), and indicated that the NBS would decline in its ability to respond to changes in pH as it completed its formation. Based on this phenomenon, it can be hypothesized that NBS is very sensitive to changes in the surrounding environment at the initial stage of formation and has a weak resistance to pH changes in the external environment, but this resistance will gradually increase as NBS tends to stabilize.

2.3.2. Effect of temperature on the stability of NBS

Temperature is a very important physical parameter for a solution and profoundly affects the amount of dissolved gases in a solution. Li et al. (2021) reported that NBS tended to be more balanced at higher temperatures. When the temperature of the NBS suspension was increased from 25° to 40°, an evolution curve of the NBS distribution with temperature and time was obtained (Fig. 10a). While the temperature falls behind to room temperature 25°, the radius of the bubbles decreased from 128 nm to about 66 nm, and cooling allowed the NBS size to return to the same distribution as before (Fig. 10b), which shows

that the growth and contraction of NBS is a reversible physical process. And according to further experimental results, there exists a transition temperature T_c within the temperature range of 40°C-50°C, less than this T_c the diffusion coefficient δ of the bubbles decreases rapidly as the temperature rises and the bubbles undergo contraction; at temperatures greater than T_c the bubbles will expand again. This transition temperature T_c is related to the preparation method and measurement configuration of the NBS. In their report it is also illustrated that the zeta potential of NBS has a strong dependence on temperature, probably due to the loss of charge of NBS caused by the low temperature environment. Previously, when Xu et al. (2014) researched NBS's formation on surfaces, they discovered that more NBS were noticed at high temperatures than at low temperatures, and attributed the phenomenon to the higher gas saturation under high-temperature conditions, which favors the formation of NBS.

Even though it is possible to increase the stability of NBS by means of warming, it is still necessary to take into account the properties associated with the surface of the particles on which NBS is adsorbed. According to Zhou et al. (2022a), it was reported that NBS generated using the warming method could not be stably adhered on the surface of hydrophilic glass beads because the contact area of the hydrophilic glass beads with NBS was too small compared to the rough glass beads such that the overall increase in the area of NBS adherence was less than 1%, resulting in an unstable adhesion of NBS. However, it is certain that the effect of temperature on NBS plays a key role in the stability, because NBS is still a form of existence of bubbles, the temperature affects dissolved gases' content mainly in water (Li and Zhang, 2022b), and the bubbles can not be detached from the dominant role of the gas on itself.

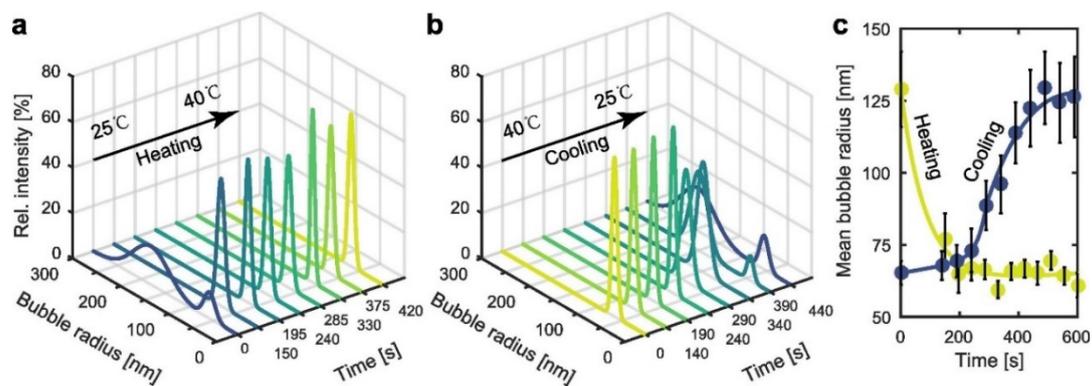


Fig. 10. Evolution of NBS with time during (a) heating (from 25°C-40°C) and (b) cooling (from 40°C-25°C), respectively. (c) Evolution of the mean radius of bubbles over time corresponding to warming and cooling (Li et al., 2021)

2.4. Theory of nanobubble stability

There are still controversies about the stability of NBS, but various theories have been used to try to explain this phenomenon in order to reveal the potential stabilization mechanism of NBS, including the contact line pinning theory (Liu and Zhang, 2014; Dockar et al., 2020), the dynamic equilibrium theory (Brenner and Lohse, 2008; Ma et al., 2021), the charge stabilization theory (Nirmalkar et al., 2018a), and the impurity contamination theory (Ducker, 2009). However, these theories still have some shortcomings in explaining the stability of NBS, and further research is needed regarding this aspect. In order to further understand the stability of NBS, it is necessary to review some popular theoretical doctrines about the stability of NBS.

2.4.1. Three-phase contact wire nailing theory

Zhang et al. (2013) and Weijs and Lohse (2013) proposed a three-phase contact line pinning theory for NBS stability in 2013. The essence of the three-phase contact line pinning theory is that when NBS is adsorbed on a solid surface, it is stably pinned to the solid surface by a contact line with the interface of the medium (this contact line is related to the surface roughness and inhomogeneity). The pressure inside the NBS will act as a resistance to further changes in the NBS (e.g., diffusion), creating a negative pressure feedback to maintain the size of the contact radius r (Fig. 11).

It was previously reported that the Young-Laplace model still holds at the nanoscale scale (Liu and Cao, 2016)

In solution when NBS is present on the surface of a solid with a bubble radius of R .

$$P = \frac{2\gamma}{R} + P_0 = \frac{2\gamma}{r} \sin \theta + P_0 \quad (5)$$

$$R = r / \sin \theta \quad (6)$$

where P is the internal pressure of NBS, γ is the gas-liquid interfacial tension, R is the radius of a bubble, P_0 is the radius of a bubble, θ is the bubble contact angle.

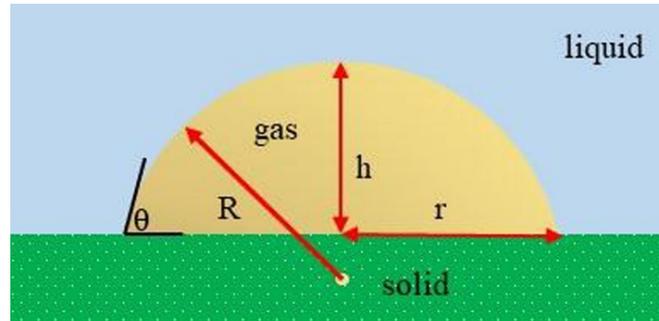


Fig. 11. Schematic diagram of three-phase contact wire nailing theory (Tao, 2022)

When diffusion of NBS occurs, its bubble contact angle decreases. Calculated from Eq. (5), the pressure P inside the bubble decreases as θ decreases. thereby delaying the further contraction of NBS to maintain the length of the contact radius r . So, the theory shows that the internal pressure of the NBS acts as an impedance effect, which hinders the rupture of the NBS and maintains its stability in the case that the NBS is reduced in internal gas.

A lot of researchers have confirmed the three-phase contact line's correctness pinning theory through their studies in recent years. Some reports pointed out that under the action of flotation chemicals (especially the trapping agent), it will cause the inhomogenization of the mineral surface, which will cause the pegging effect and promote the formation of NBS (Owens et al., 2018) (Fig. 12), and it can be observed that there is no significant effect on the height of NBS under the addition of chemicals, and the heights of NBS under the three conditions basically remain the same. According to previous reports, flotation chemicals had no effect on the surface tension of NBS, which was constant in the presence of added chemicals (Zhang et al., 2006; Ducker, 2009), so it was hypothesized that the effect of the trapping agent on the NBS was through the enhancement of the pinning effect of the NBS, which increased the bubble density while improving the stability of the bubbles. The formation of NBS was subsequently analyzed from the results of Wang et al. (2019a) who observed NBS by AFM, which showed that NBS's formation is affected by the effects from pinning effect and surface tension.

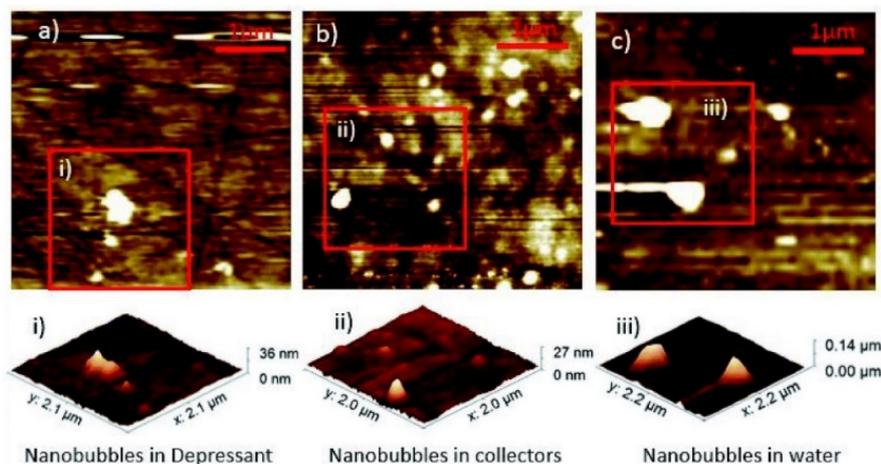


Fig. 12.(i)-(iii) AFM topographic images of NBS present on the dolomite surface in inhibitor (a), trap (b) and water (c), respectively (Owens et al., 2018)

2.4.2. Dynamic equilibrium theory

Brenner and Lohse (2008) proposed a gas-rich layer's existence around the NBS, where gas enters the bubbles from the bubble contact line and makes up for gas that escape from surface of the NBS by injecting it up, thus creating a dynamic equilibrium stabilizing the NBS (Fig. 13a). For larger size lumpy NBS, in solution due to gas escape and gas diffusion processes occurring simultaneously, before the formation of a stable NBS the degree of gas injection gradient are faster than the gas escape, but the effect of gas diffusion over time in the weakening, when the intensity of the two effects are the same, the gas exchange equilibrium is reached inside the bubble, the NBS will tend to be stabilized. Initially, when the inlet volume is larger than the exhaust volume, this will cause changes in the contact radius and contact angle, and as both of them change towards a decreasing trend, the NBS will spontaneously return to the initial state. Similar to the pinning theory, this is a form of negative feedback.

The inflow NBS gas volume is:

$$j_{in} = \frac{2\pi sRD}{-\tan(\pi-\theta)} \quad (7)$$

$$j_{out} = \pi RD \left(1 - \frac{C_{\infty}}{C(R)}\right) \quad (8)$$

Gas outflow volume:

$$C(R) = C_0 \Delta P / P_0 \quad (9)$$

where D is the gaseous diffusion constant, s is the potential attraction, R is the radius of a bubble, C_{∞} is the the gas concentration away from the nanobubbles, $C(R)$ is the gas concentration at the surface of the bubble, C_0 is the Gas saturation concentration corresponding to a gas pressure of P_0 , ΔP is the Laplace force.

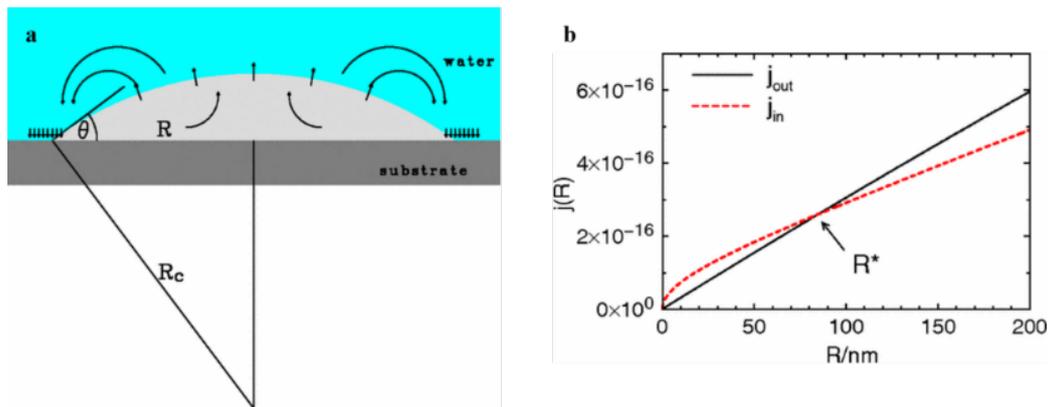


Fig. 13. (a) Schematic diagram of simultaneous gas inflow and outflow of NBS in solution, (b) gas escape, gas compensation versus bubble radius (Brenner and Lohse, 2008)

From Fig. 13b, it can be seen that the gas inlet is slightly higher than the exhaust at the early stage of bubble formation, and as the bubble radius grows, the gas escape intensity is gradually larger than the gas injection intensity, and the bubble radius R will be maintained at a stable value when $j_{in} = j_{out}$ and the bubble reaches dynamic equilibrium.

Based on the recognition of the effect of gas solubility on bubbles, in Wang et al.'s (2019a) study of NBS lifetimes with different dissolved gases (including O_2 NBS, CO_2 NBS, and N_2 NBS), they concluded that NBSs formed from highly soluble gases may be smaller. Assuming that their conclusions are correct, the gas diffusion constant D will be larger for NBSs composed of highly dissolved gases, and the NBS will stabilize more quickly.

MD simulations by Wu et al.(2019) showed that the gas diffusion coefficient can be improved by applying an applied electric field. Zhou et al. (2022b) reported that the instability of BMBS (Bulk-microbubbles) has a high potential to lead to rapid changes in the concentration of dissolved gases in water. Therefore, based on this theory, the stability of NBS depends to some extent on the balance between gas solubility and internal bubble gas overflow and spillage, and based on the previously discussed effect of temperature on NBS, it can be understood that high temperature reduces the gas

saturation concentration C_0 of NBS, which results in a decrease in the gas surface concentration $C(R)$, leading to an acceleration of the process of stabilization of NBS. However, there are still some unexplained phenomena in this theory, such as the energy source of this effect is not yet clear in order to maintain this dynamic equilibrium of gas inflow/outflow between NBS's inside and the outside globe at ambient temperature, and the dynamic equilibrium effect may be unstable due to the difference in the contact angle of different contact surfaces as well as the inhomogeneity of the surfaces, when the same gas is inside the NBS. Therefore, although the theory can be used to explain some of the findings, the theory itself is still imperfect. Yasui et al. (2015) considered van der Waals forces between gas molecules inside NBS and adsorbed surfaces on the basis of the original dynamic equilibrium theory, which can be used to explain the presence of NBS adsorbed on hydrophilic surfaces. Recently Ma et al. (2021) developed a dynamic equilibrium model of NBS on the surface of nano-electrode by combining theoretical analysis with MD simulation, and concluded that the dynamic properties of NBS are closely related to the changes of gas solubility and solute concentration based on the performance of NBS in maintaining the stability of the nano-electrode surface. The modification and extension of the basis of this theory will expand the application scope of the dynamic equilibrium theory.

It is worth mentioning that the explanation of the stability is basically related to the visualization parameters such as equilibrium bubble radius and equilibrium bubble contact angle, all of which ultimately result in the transformation of the contact radius into a definite value in a complex environment, so that it remains constant between itself and the contacting surface, to make sure that the NBS is stably adsorbed on the particles' surface. In recent years, with the deepening of the understanding of the stability of NBS, some theories have been supported by experimental and modeling data, and with the theoretical analysis and experimental research carried out by the researchers, the theory of the stability of NBS has become more and more perfect. However, the popular theories have not yet been able to accurately explain the stability of NBS, and there are still controversies, and in some special cases these theories can't explain the block NBS well, so there is no accurate and uniform answer for the high stability of NBS.

3. Current status of NBS applications in particle flotation

In froth flotation, hydrophobic particles tend to adsorb onto the froth, forming a froth-particle aggregate that is further recovered as a concentrate. Whether froth flotation can recover particles efficiently depends mainly on the three behaviors of collision, adhesion, and stripping between the froth and particles in the flotation cell (Fig. 14).

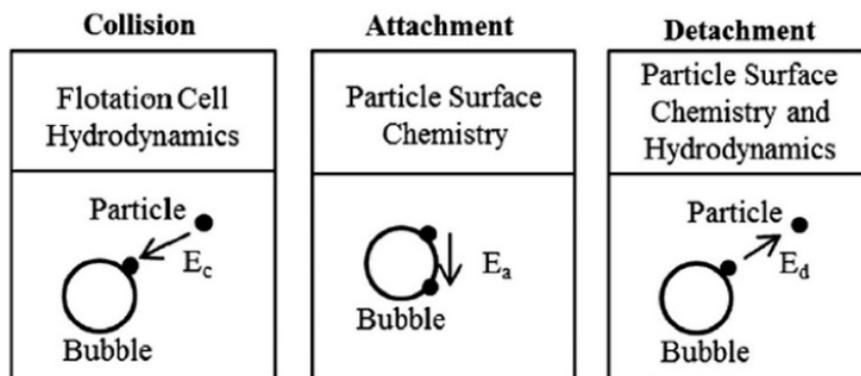


Fig. 14. Three processes of particle-bubble interaction (Wang and Peng, 2014)

Recovery of particles using NBS can significantly improve the flotation efficiency (Sobhy and Tao, 2013a,b; Ahmadi et al., 2014; Calgaroto et al., 2015; Rosa and Rubio, 2018; Chang et al., 2020). Zhou et al. (2020b) increased the flotation rate k by almost 1/4 after using NBS in the recovery of dolomite minerals using DDA. According to the first-order model (10), which is commonly used in flotation kinetics:

$$\varepsilon = \varepsilon_{\infty}(1 - e^{-kt}) \quad (10)$$

where ε is the flotation efficiency, ε_{∞} is the theoretical maximum recovery rate, k is the flotation rate constant, t is the time spent in flotation.

According to existing studies, NBS can selectively adsorb on the surface of hydrophobic particles, and its impacts on particles include, but are not confined to, increasing the particle surface's hydrophobicity (Chang et al., 2020; Zhang et al., 2021b), thereby promoting bubble-particle interactions and improving flotation recovery. Some scholars claimed that the stability and probability of bubble-particle attachment can be improved by NBS in flotation systems by increasing the contact angle at the bubble-particle interface (Fan and Tao, 2008; Fan et al., 2010a; Sobhy and Tao, 2013b). According to Chen et al. (2022), NBS that is adsorbed on particles' surface can enter and stay in the voids on the particle surface, thus expanding the particles' hydrophobicity. Zhang et al. (2021b) reached a similar conclusion in their study of the mechanism of NBS-enhanced lignite flotation. It has been shown that NBS can simultaneously help the attachment between nanoparticles and macrovesicles (FAN et al., 2010a-d). In the study of Nazari and Hassanzadeh (2020), DDA-NBS generated by hydrocavitation using DDA as a frothing agent increased the flotation rate constant k and final recovery R_{max} of coarse quartz particles by 22% and 21%, respectively. Sobhy and Tao (2019), in their study of the effect of NBS on the stability of conventional flotation froth in froth flotation columns, demonstrated for the first time that flotation froth's stability was well improved in the presence of hydrophobic particles and NBS at contact angles greater than 85°.

3.1. Improving flotation efficiency by reducing bubble size

Bubble size is a very significant physical parameter in minerals' general positive flotation process. And the bubble rise rate is related to the bubble size. Reducing the bubble size can not only increase the specific surface area of the bubble, so that the bubble has more contact area when capturing the particles, and reduce the bubble rising speed, prolonging the reaction time of the bubble and particle contact. Therefore, the flotation efficiency can be improved by reducing the bubble size. Hassanzadeh et al. (2016) investigated the effect of bubble size on the collision efficiency of chalcopyrite flotation by predicting the collision probability of chalcopyrite particles with different bubble diameters through two collision models, GSE and Schulze, and the prediction results showed that the collision probability of particles decreases with the increase of the bubble size. Reis et al. (2019) utilized different sizes of bubbles to conduct apatite flotation experiments and found that the small bubbles were completely encapsulated by the ore particles, but the final recovery was lower for this size of bubbles, which was due to the small uplift force of the small bubbles, and a part of the bubble-particle aggregates formed settled. This suggests that small bubbles can be used for reverse flotation in a particular situation and the recovery may be better than in forward flotation.

Improving flotation efficiency by reducing bubble size has attracted attention. Recently Li (2023) achieved efficient separation using small bubbles with a significant reduction in particle density when separating pyromolybdenite with size fractions of 150-450 μm and 450-700 μm . Shadman et al. (2023) put ultrafine bubbles into the rougher flotation of zinc minerals and lead. The experimental results showed that the introduction of ultrafine bubbles led to an increase in lead-zinc recovery by 7.41% and 1.22%, respectively. In conclusion, the small bubbles that were produced by reducing the bubble size will improve the particles' flotation kinetics. Trapping agent, slurry properties, and air flow rate all affect the bubble size to some extent, but one of the factors that have a deeper influence on the bubble size is the frothing agent. The use of suitable frothing agent and increasing the concentration of frothing agent can reduce the bubble size and improve the flotation recovery (Wang et al., 2020). The recovery of fine particle flotation produced in the milling system is limited by the particle-to-bubble diameter ratio, resulting in a low probability of bubble-particle collision. In contrast, the smaller the bubble size, the higher the collision efficiency in the same particle size range (Zhang et al., 2021a). Therefore, one of the reasons for using microbubbles to improve fine-grain flotation recovery is that microbubbles increase the probability of bubble-particle collision.

3.2. Mechanism of NBS enhancement of flotation collision probability

Among the three sub-processes of bubble-particle attachment, the study of collision probability is the most studied one. In complex turbulent environments, there is some trouble in the collision between particles and bubbles. The collision probability between bubbles and particles is an important parameter for froth flotation, and generally in the conventional flotation process, the particle collection efficiency

(11) depends largely on the degree of collision between particles and bubbles. The formula for the collision probability is shown in (12) (Tao, 2005; Miettinen et al., 2010).

$$P = P_c P_a (1 - P_d) \quad (11)$$

$$P_c = \left(\frac{3}{2} + \frac{4Re^{0.72}}{15} \right) \left(\frac{D_p}{D_b} \right)^2 \quad (12)$$

where P is the collection probability, P_c is the collision probability, P_a is the attachment probability, P_d is the probability of disengagement, Re is the Reynolds number (ratio of inertial forces to viscous forces in fluid mechanics), D_p is the particle size, D_b is the bubble size.

From equation 12, it can be seen that decreasing the bubble size can increase the collision probability, thus increasing the particle recovery rate. On the other hand, particles can also increase the collision probability if they aggregate to form agglomerates during the flotation process, which increases the apparent size of the particles. Recent work by researchers has shown that NBS enhances the attraction between mineral particles and makes particle aggregation more pronounced (Zhou et al. 2020b), an effect that also includes ultrafine particles of smaller size ($d < 10 \mu\text{m}$) (Zhou et al., 2020a).

3.2.1. NBS affects particle flotation via zeta potential

According to the classical DLVO theory, the double electric layer on bubbles' surface plays an important role in the interactions between particles and bubbles, and for NBS the surface zeta potential in solution is a significant factor that influences the electrostatic repulsion and thus is worthy of attention. NBS is normally negatively charged in water like ordinary air bubbles. However, the bubbles undergo a charge reversal phenomenon in certain salt solutions, where they shift from a negative to a positive potential. Han et al. (2004) investigated zeta potential parameters' effect on particle-bubble collisions and observed the change in bubbles' zeta potential in divalent solutions of magnesium ions and calcium, and found that bubbles were negatively charged throughout the entire pH range in Ca^{2+} containing solutions, and that positively charged bubbles appeared in Mg^{2+} solutions at $\text{pH} > 9$, and that the zeta potential increased with the concentration of Mg^{2+} and with acidic pH (Fig. 15a). They attributed the above phenomenon to the hydrolysis of $\text{Mg}(\text{OH})_2$ precipitate in magnesium solution, and the specific adsorption of hydroxylated substances, which allows the occurrence of the charge reversal phenomenon, which is in agreement with the earlier conclusions of Zouboulis (Zouboulis et al., 1992). Therefore, it is possible to achieve a higher probability of collision by changing the solution properties, which can be realized by the opposite sign of the charge of the particles and bubbles, resulting in electrostatic adsorption (Han, 2002). The results obtained by Han in his subsequent study of the zeta potential of the bubbles on the efficiency of the electroflotation of kaolin particles are also basically the same (Han et al., 2006) (Fig. 15b).

This shows that the indication of the bubbles' zeta potential is correlated with the solution pH and the ions adsorbed on the surface. This conclusion has also been experimentally verified in NBS by some researchers. Cho et al. (2005) measured the zeta potential of NBS in two solution environments, an aqueous electrolyte solution and a surfactant, for NBS and found that the zeta potential of NBS itself has a positive potential at low pH and a change in sign at high pH, suggesting that the electrical properties of the surface of NBS are changed with the adsorption of OH^- and the H^+ desorption, and the magnitude of the potential is increased by the increase of salt concentration. The positive zeta potential of NBS was also reported to decrease with increasing pH according to an earlier study (Kim et al., 2000). The magnitude of zeta potential of NBS varies in different solvents. For example, in a solution with the addition of DODAB (a double-chain cationic surfactant), the zeta potential of NBS decreased from $+40 \pm 2 \text{ mV}$ to $+20 \pm 5 \text{ mV}$ when the pH was increased from 2 to 12, and in a solution with the addition of Al^{3+} and Fe^{3+} at a concentration of 1 mM, the NBS zeta potentials were all positive in the range of pH 2 to 12 (Bui et al., 2019). Zhang et al. (2020b) also reported that the zeta potential of NBS generated using cavitation tubes at a MIBC surfactant concentration of 50 mg/L shifted from positive to negative down to -9 mV in the range of pH 3~12 adjusted with sodium hydroxide and hydrochloric acid.

This reflects the fact that competitive adsorption between molecules/ions occurs on the surface of bubbles in solution. Zeta potential is a consequence of the charge that is induced by ions' adsorption on the bubble's surface, and the adsorption pattern of ions on the surface of bubbles in solution has a

significant effect on the zeta potential of the bubbles, and the same conclusion applies to NBS as well. However, according to the prediction of Zhang et al. (2016) the occurrence of the above phenomenon may also be due to the adsorption of NBS on the surface of the particles, and the bubbles shielded some of the charges on the surface of the particles.

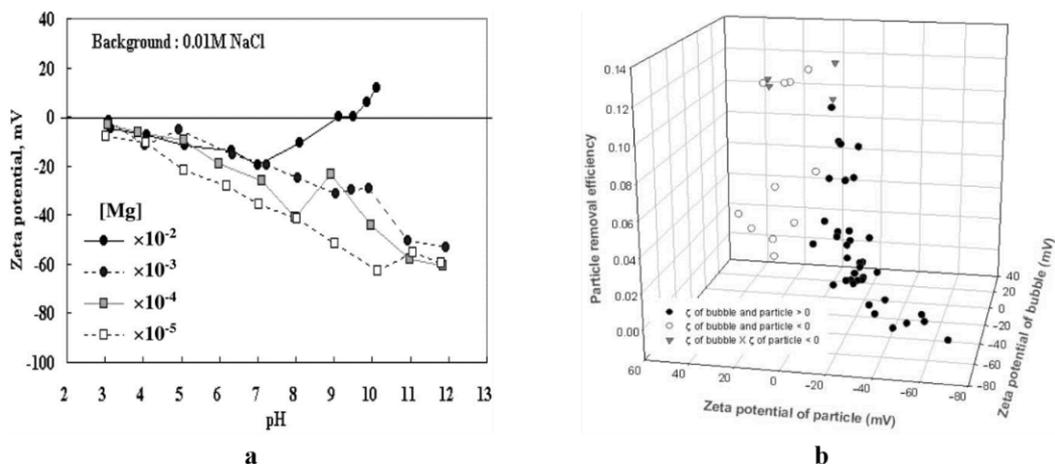


Fig. 15.(a) Variation of zeta potential of bubbles in different concentrations of MgCl_2 (Han et al., 2004) (b) Effect of zeta potential of bubbles and particles on removal efficiency in the absence of flocculation, with an average particle size of 0.1 mm for kaolinite (Han et al., 2006)

The above discussion suggests that a series of behaviors of NBS during flotation can be modulated by changing the zeta potential of NBS. Li et al. (2022d) suggested that positively charged NBS (PC-NBS) can be used to recover high ash fine coal. That was shown by the experimental results compared to conventional NBS, PC-NBS's use enhanced coal particles' aggregation and improved the combustible recovery. Similar conclusions were found in a study by Xia et al. (2019), although the bubbles used were microbubbles slightly larger in size than NBS. This positively charged bubble introduces additional electrostatic attraction and enhances the interaction with hydrophobic particles. In the work of Xiao et al. (2019b) sodium oleate was used to modulate the zeta potential of the NBS surface by adjusting the pH to affect the distribution of sodium oleate in solution, which in turn affects the amount of sodium oleate adsorbed on the surface of the NBS, which in turn leads to the effect of a change in the zeta potential of the NBS, which affects the electrostatic repulsion between the NBSs and realizes the inhibition of mutual collisions of the NBSs in solution through the electric charge.

NBS can also in turn affect the zeta potential of the particle surface, which means that the electrostatic force between two interacting particles will change due to the presence of NBS (Snoswell et al., 2003), enhancing the attachment of bubbles to particles during flotation. In a recent report, Wu et al. (2023) investigated the mechanism of NBS generated by hydrodynamic cavitation for enhanced flotation of pyrite. Under hydrodynamic cavitation conditions, in both high and low dosages (20 mg/L; 0.1 mg/L) of SAX (sodium amyl xanthate), the SAX ions remaining after adsorption on the pyrite surface appeared to have different trends on pyrite zeta potential with the increase of treatment time (Fig. 16a). This is due to NBS's adsorption on the surface of pyrite, which leads to a protective bubble-water layer's formation on the surface of pyrite covering part of the particle surface charge. Alam et al. (2022) also reported the accelerated reduction of the negative potential of pyrite surfaces by NBS. Chongliang et al. (2023), in his study of the mechanism of NBS-enhanced flotation of fine-grained graphite showed that the presence of NBS adsorption on the surface of graphite with a zeta potential decreased more significantly than that of ordinary graphite. This may be due to the fact that the presence of NBS on the surface of the particles during the flotation process decreases the zeta potential and reduces the electrostatic repulsion between the particles, which is conducive to particle agglomeration and also promotes the adhesion between the agglomerated particles and the flotation froth, which improves the recovery of froth flotation. Similar results were reported by Wang et al. (2022). The findings of Ma and Tao (2022) on the relationship between NBS and graphite were also almost identical and they found that NBS could also recover ultrafine graphite efficiently while developing a novel mill and column

flotation process. Prior to this Tao also reported a mechanistic study of NBS-enhanced anticathodic flotation of hematite, which significantly improved the flotation performance of hematite after the introduction of NBS (Tao et al., 2021). Lu (2019), after molecular dynamics (MD) simulation of NBS, suggested that the decrease in the negative potential of the particle zeta was favorable for froth flotation. According to the existing research work, the phenomenon of NBS decreasing the zeta potential of particle surface is not limited to pyrite and graphite, but similar phenomena exist in kaolinite, rutile, and the more hydrophilic muscovite (Fig. 16(b)-(d)) (Wang et al., 2019; Zhou et al., 2019; Zhang et al., 2021c; Zhang et al., 2022).

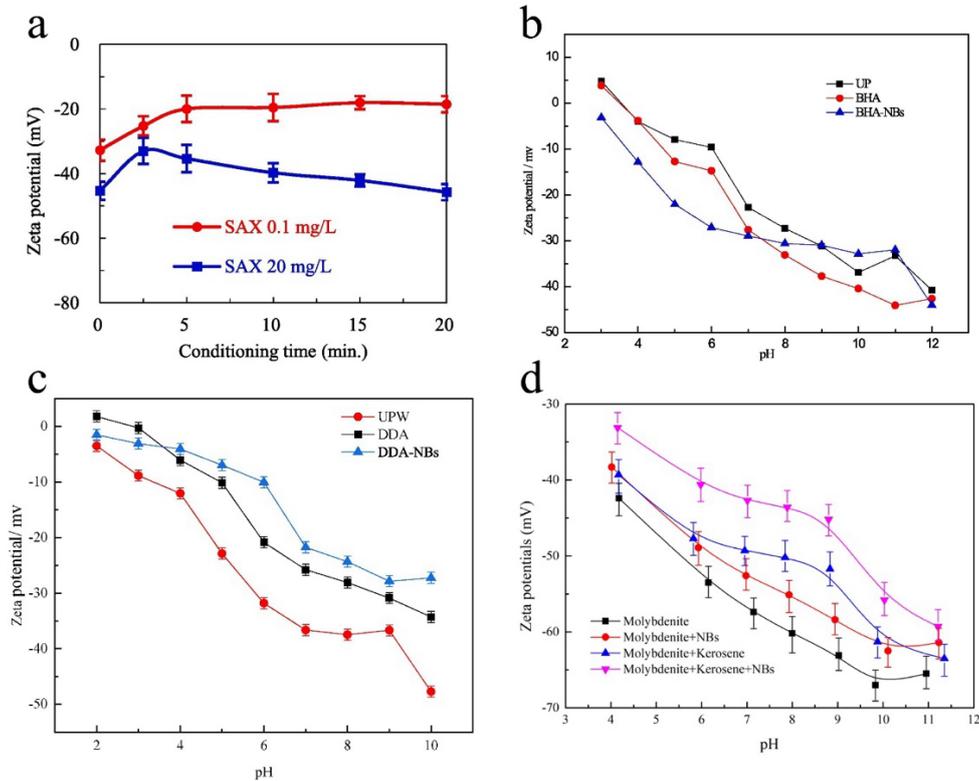


Fig. 16.(a) Effect of hydrodynamic cavitation time on zeta potential of pyrite surface at SAX dosages of 0.1 mg/L and 20 mg/L (Wu et al., 2023). (b)-(d) Variation curves of the effect of NBS on the zeta potential of different ore surfaces as a function of pH, (b) Effect of BHAs and NBs on the zeta potential of rutile particles suspension system (Zhang et al., 2021c), (c) Changes in zeta potential of white mica under different pH conditions in three liquid environments: ultrapure water (UPW), DDA solution and DDA+NBS solution, respectively. (Chen et al., 2022), (d) Zeta potential of molybdenite surfaces in the presence and absence of kerosene/NBS (Wang et al., 2022)

However, Li et al. (2022a) investigated the interaction of NBS with hydrophobic coal particles of different particle sizes and found that NBS had almost no effect on the zeta potentials of particles of 1.4 ~ 1.5 kg/L and particles of lower densities, and they attributed this phenomenon to the fact that the NBS was very close to the zeta potentials of the particles, which left the zeta potentials of the particles unshifted, or it could be the case that the particles had too small a surface of amount of NBS is too small. The latter speculation should be based on the finding in the experiment that the contact angle of the coal decreased from 81.5° to 22° when the density of the coal was increased from -1.3 kg/L to +1.8 kg/L (which may be due to an increase in the hydrophilic minerals in it with the increase in the content of the samples), which resulted in a decrease in the hydrophobicity of the coal, making the adsorption of the NBS weaker.

Zhang et al. (2019) investigated the interaction of positively charged colloidal nanoparticles with supersaturated gas solutions using an electrophoretic probe to observe the change in the surface charge of nanoparticles at different concentrations in NBS solution; when the nanoparticle concentration is high, the particles are positively charged; as the concentration decreases, the zeta potential will reach the point of zero charge, and the particles will switch from a positive charge to a negative charge. This

symbolizes the formation of nanoparticle-NBS structure due to the nucleation of the gas generating corresponding nanoscale bubbles that cover the particle surface. It was also found that when the potential difference between the bubbles and the particles was zero, it was observed that aggregates with larger particle size were still present in the solution. This indicates that the NBS attached to the particle surface when the electrostatic repulsive force disappears may possess an attractive force over a certain distance, which makes the particles agglomerate and improves the flotation performance. The percentage of this facilitating effect of NBS is not yet clear, and there is some controversy as to whether it can be explained by the capillary force of NBS. To investigate this phenomenon, Azadi et al. (2020) measured the force between a hydrophobic wafer substrate and hydrophobic silica particles, and the magnitude of the force was measured by the glueprobe technique along with the results of AFM imaging (Fig. 17) while eliminating the effect of the capillary force of NBS. It was observed that the attraction between the hydrophobic surfaces weakened along with a decrease in the dissolved gases' concentration in the aqueous solution (the salt concentration controls the solution gas content). The results of this experiment support the idea that dissolved gases determine to some extent the attraction between hydrophobic surfaces. The current explanations for this mechanism speculate that it may be due to the short-range force of mutual attraction that is present on the hydrophobic surfaces themselves, or due to the capillary force of the NBS, or it may be a synergistic effect of the two. The capillary forces mentioned will be discussed in the next section.

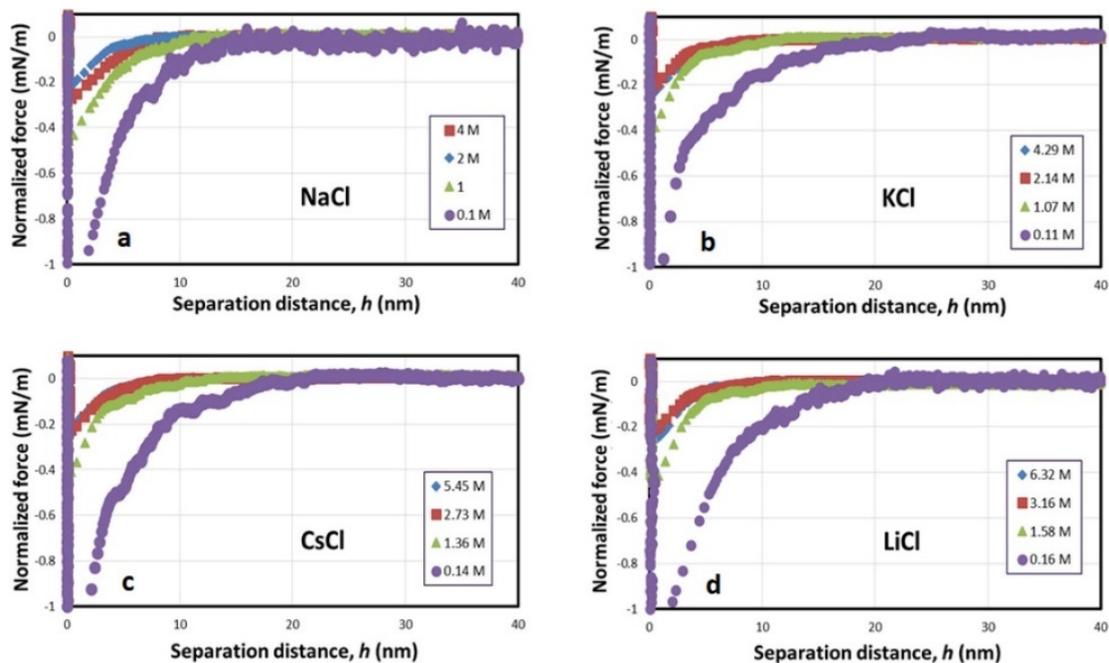


Fig. 17. Distribution of force profiles in solutions of different solutes of NaCl, KCl, CsCl, LiCl at different concentrations (Azadi et al., 2020)

Through the above discussion of the mechanism of NBS promoting particle collision probability through zeta potential, the following conclusions can be drawn: firstly, due to the phenomenon of charge reversal of the surface zeta potential of NBS under the influence of external factors, thus realizing that the sign of the surface charge is opposite to that of the particles, the electrostatic attraction between each other will be enhanced (González-Tovar and Lozada-Cassou, 2019; Zhang et al., 2019) (this is in line with the idea initially proposed by Han et al. (2004) in 2004 proposed to improve particle recovery by adjusting the solution environment so as to form positively charged bubbles, which was also verified by the experimental results of the subsequent researchers); secondly, when NBS that was adsorbed on the particles' surface will also reduce zeta potential's magnitude on the surface of the particles, which will decrease the electrostatic repulsion between the particles and advance the agglomeration between the particles (Michailidi et al., 2020; Kyzas et al., 2021; Zhang et al., 2022). An in-depth understanding of the relationship between NBS and zeta potential will be beneficial for the development of new flotation modulation techniques regarding NBS.

3.2.2. Capillary force/bridging effect of NBS

When NBS are selectively adsorbed on the surface of particles, they attract particles with NBS adsorbed on the same surface to each other such that clusters of particles are formed. One of the reasons for this is the presence of NBS bridging, whereby the aggregation of NBS forms gas capillary bridges (a phenomenon that further develops capillary forces), similar to the formation of a bridge linking the particles together, called bridging (Attard, 2003; Hampton et al., 2008).

In 2010 Hampton and Nguyen in their review of NBS related capillary force experiments noted that NBS can induce long range hydrophobic proximity between particles due to this capillary force. (Hampton et al., 2010). They previously gauged the NBS capillary force (NBCF) between a hydrophobic silica colloidal probe and a hydrophobic silica wafer applying AFM, and detected an attractive force between the NBS attached to the particle surfaces, making the distance between particles smaller. The formed capillary bridges promoted the aggregation of particles (Fig. 18).

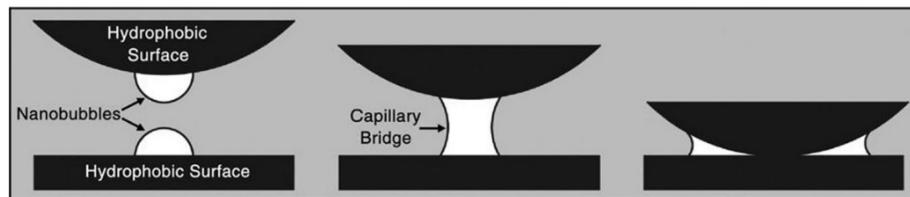


Fig. 18. NBS promotes the proximity of two hydrophobic surfaces to each other and acts as a bridge between them (Hampton et al., 2010).

The strength of this capillary force is somewhat related to the hydrophobicity of the particles. The more hydrophobic the particles are, the more likely they are to aggregate into clusters in the NBS water and the stronger the bridging effect is, and conversely this effect is not evident between particles with weak hydrophobicity (Liu et al., 2021; Ma et al., 2022a). However, it should be noted that this bridging effect/capillary force refers to the interaction between NBS on the surface of the particles rather than NBS acting with the surface of the particles (Knüpfer et al., 2017; Li et al., 2020b). This could explain the phenomenon of Wang et al. (2019a) who found that the NBS was adsorbed as an associative layer on a fully disintegrated molybdenum surface when observed using AFM. The shape of the capillary force is strongly related to the contact angle of the adsorbed surface. According to the capillary force equation (13) shows that when the contact angle θ is less than 90° the bonding force is repulsive, preventing the particles from aggregating, and greater than 90° it is gravitational, strengthening the contact between the two surfaces (Fig. 19). However, according to Hampton capillary forces are not an effect due to particle hydrophobicity (Hampton et al., 2010).

The aggregated particle bodies will be more easily captured by the flotation bubbles and rise into the concentrate froth zone for easy recovery. Tao and Sobhy (2019) imaged NBS using AFM and found that when hydrophobic surfaces are in close proximity to each other, capillary bridges formed by interactions between the NBS bring flotation bubbles and both surfaces of the particles in contact with each other, and are more prone to bubble-particle formation than particles without encapsulated NBS Aggregation. Ding et al. (2020) measured the specific values of capillary forces induced by NBS on the particle surface. The values of the force to separate the particles from the bubbles were 9.88 and 11.59 μN in the presence and absence of NBS, respectively, when the particle contact angle was 105° . Their results indicated that the effect of NBS made the formed particle aggregates more stable.

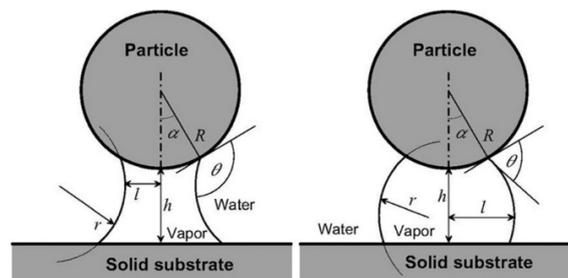


Fig. 19. Concave (left), Convex (right) Capillary Bridge (Hampton and Nguyen, 2009)

$$\Delta P = \frac{2\gamma \cos \theta}{r} \quad (13)$$

where γ is the liquid surface tension, r is the capillary tube radius.

The effect of NBS on particle aggregation was further verified by the work of researchers. The results of Chang et al. (2020) and Li et al. (2022a) showed that NBS caused coal particles to agglomerate on their own due to its preferential adsorption on the surface of the coal particles, expanding the difference in hydrophobicity between the coal and the ash. Pourkarimi et al. (2021) utilized hydrodynamic cavitation-generated NBS to improve fine-grained phosphate ore. The flotation recovery was found to be enhanced by NBS, which improved the attachment between particles and bubbles, and ameliorated the interaction between bubbles and particles while the adsorption of flotation trap on flotation particles' surface was reduced. Xiao et al. (2018) showed that the use of NBS could flocculate and precipitate Pb particles, and the flotation recovery of the particles could be increased up to 90%. Nazari et al. (2023) investigated the separation of Li-e batteries from waste cars in the presence of microbubbles, the hydrophobicity of the anode active material in the electrode material after roasting in the presence of NBS was enhanced and the amount of agent was reduced. The results showed that the recovery and grade of the electrode active material were improved in the NBS's presence. Li et al. (2022c) investigated the improvement of particle flotation performance by hydrodynamic cavitation-generated NBS in terms of zeta potential, slurry particle size, and particle surface coverage, and confirmed that the enhancement of the probability of collision and attachment of the hydrophobic particles to the bubbles was attributed to the facilitating effect of NBS. However, this bridging interaction may be destroyed by ultrasonic waves (Yasuda et al., 2019; Li et al., 2020a). The above results indicate that when NBS adsorbs on the particle surface, the surface properties of the particles change, and this change tends to be beneficial to the attachment between particles and bubbles, and it is important to explore the interaction between NBS and particles to enhance particle flotation.

Through the discussion of the mechanism of NBS to enhance particles' flotation performance, NBS can affect the zeta potential of the particle surface, as well as promote the aggregation of particles and increase the apparent diameter of particles through the formation of NBS. However, there may be other mechanisms by which NBS affects particle flotation at present, and there is no consensus on the mechanism by which NBS promotes particle aggregation and enhances bubble collision probability.

3.2.3. Study on the effect pattern of NBS on the flotation effect of coarse/fine particles

The function of NBS to improve particles' flotation performance has been confirmed in a lot of researches. However, in large particle/aggregate flotation, NBS acts more as an auxiliary flotation (Oliveira et al., 2017). The assisting mechanism is shown in Fig. 20.

Although NBS can be stably adsorbed on the surface of coarse particles, its carrying power makes it difficult for coarse particles to rise to the surface. Therefore, when using NBS for particle flotation, the nature of the particles themselves as well as the match between NBS and the target particles need to be

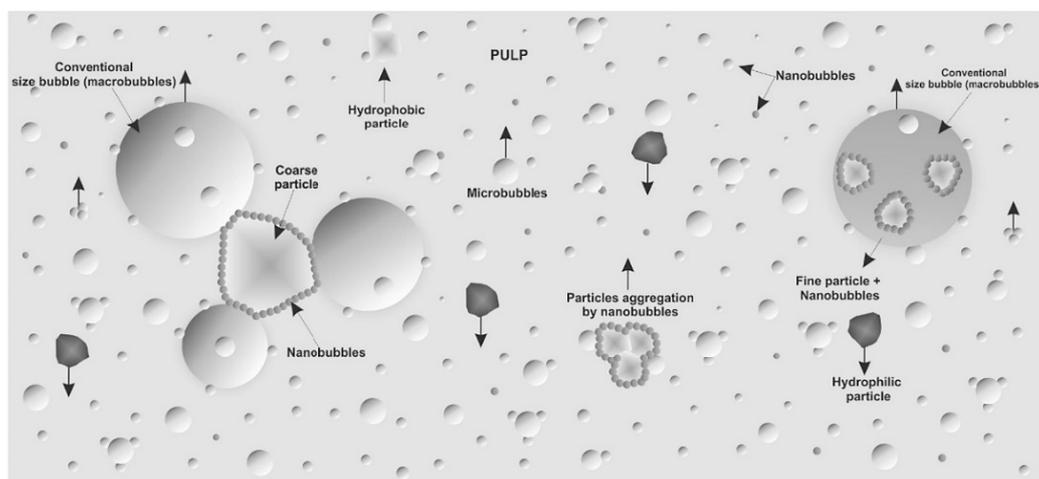


Fig. 20. Diagrammatic representation of the main mechanisms involved in the auxiliary role of NBS in particle flotation processes (Rosa and Rubio, 2018)

considered (Li, 2023). Everyone knows that ultrafine particles and microfine are difficult to be recovered by conventional froth flotation because of bubble-particle collisions' low probability. Zhang and Seddon (2016) suggested that in complex particle systems, lumped NBS can enhance the re-nucleation of gases in solution on the surfaces of particles without attached NBS. And according to previous explorations, NBS will increase the probability of collision with particles thus forming particle agglomerates. Therefore, the use of NBS for flotation of fine/ultrafine particles is a relatively suitable choice (Zhou et al., 2016). The use of NBS can be associated with smaller levels of froth flotation compared to normal froth flotation.

Generally speaking, the flotation rate of particles within the range of 20~150 μm is fast, and the recovery rate of particles exceeding this range decreases sharply. When the particle size > 150 μm , the particles are easily separated from the particle-bubble aggregates under the action of turbulent flow field. Below 20 μm , the inertia force gradually decreases and viscous resistance begins to play a dominant role. The fact that the particles are too small and tend to follow the fluid flow also leads to a generally low recovery of fine/ultrafine particles, as the particles do not easily contact and adhere to the flotation bubbles. It can also be concluded in Eq. (12) that too small particle size will lead to a decrease in particle-bubble collision probability. Zhou et al. (2020a) modeled two interactions between NBS and ultrafine coal particles based on the E-DLVO theory (Fig. 21). The modeling results and calculation show that the absolute value of the total energy between NBS and NBS is always greater than the energy's absolute value between ultrafine coal particles and NBS, and the energies between NBS and ultrafine coal particles are all negative. According to the DLVO theory, the behavior of NBS and ultrafine coal particles in this case shows mutual attraction. Model I also explains well the strong interaction between NBSs (capillary forces between NBSs) mentioned before.

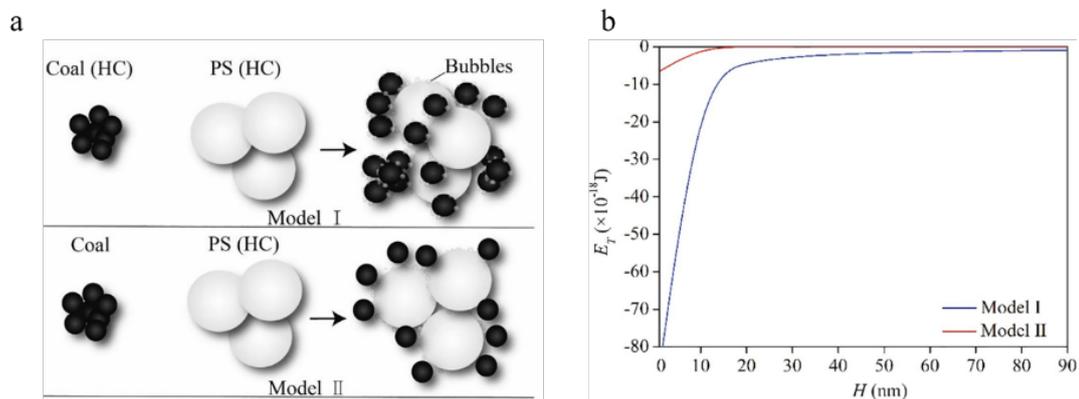


Fig. 21. (a) Two models of ultrafine particles interacting with NBS during cavitation (Model I: carrier flotation under HC pretreatment; Model II: with polystyrene fine particles acting as carriers in flotation). (b) E-DLVO interaction energy of the two models (Zhou et al., 2020a)

NBS has a significant effect on the recovery of fine/ultrafine particles by flotation. Calgaroto et al. (2016) were the first to publish results related to the use of NBS for particle flotation. Amine precipitates' micrographs were taken in the absence or presence of NBS in water using an optical microscope (Fig. 22), showing the aggregation of amine precipitates by NBS. Their experimental results showed that under NBS, amines were effectively aggregated to precipitate and float, and the residual amine concentration in the water decreased from the original 25 mg/L to 6 mg/L, and the removal effect could reach 80%. It was more effective than the use of MBS (MBS rose too fast resulting in the inability to properly collide and adhere to the amine precipitates, and MBS rose too fast resulting in the rupture of some of the precipitates). And in a later report (Calgaroto et al., 2015), it was indicated that the use of NBS could lead to an increase in flotation recovery of quartz fines/super quartz fines by almost 20-30%, because the use of NBS would increase the contact angle and aggregation effect of these two types of particles.

Zhang et al. (2023) reported that the combined effect of NBS and mixed anion/cation trap will further promote the recovery of fine lithium mica particles. The anionic/cationic traps can improve the stability of NBS, while NBS can promote particle flocculation and improve the contact angle of the particle

surface. In their experimental results, the settling efficiency of microfine lithium mica particles can be maximized from 67.65% to 71.67%. It is summarized that NBS has an unstable promoting effect on the mixed anion/cation trap, which promotes the flocculation of fine lithium mica and improves the settling efficiency of the samples.

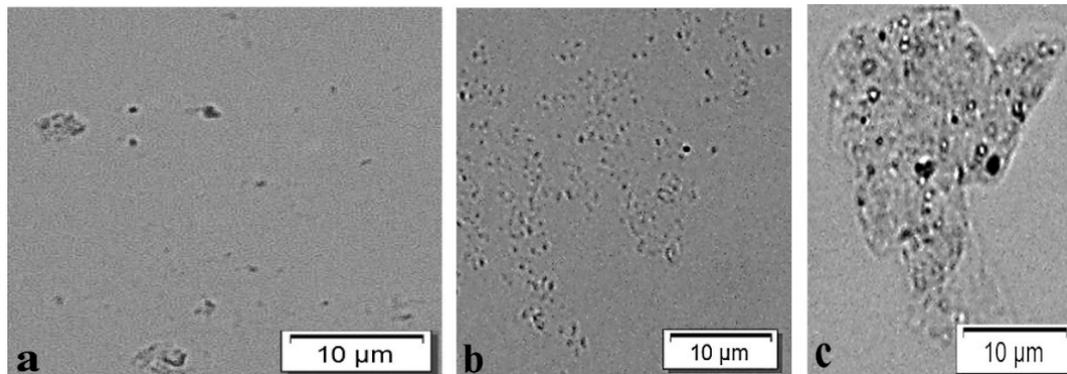


Fig. 22. Micrographs of amine nanoprecipitates at a concentration of 500 mg/L decyltrimethyl ether amine at pH 10.8: (a) nanoprecipitates without NBS (40-500 nm); (b) nanoprecipitates of aggregated NBS (40 ~ 500 nm); and (c) amine suspension precipitation with captured NBS (Calgaroto et al., 2016)

It has been documented that the presence of nanoparticles will enhance the nucleation of NBS, thus increasing the concentration of NBS. Xiao et al. (2019a) reported that the concentration of NBS tended to increase after the injection of gas into a solution pre-spiked with titanium dioxide nanoparticles because the gas undergoes a non-homogeneous nucleation process on the surface of the particles that is more prone to the formation of NBS. Titanium dioxide nanoparticles were also found to enhance the stability of NBS. According to recent MD simulations (Bird and Liang, 2023), even between two hydrophilic surfaces, the convex capillary bridges formed by NBS on their surfaces have the same ability to generate mutually attracting NBS capillary forces, which improve the aggregation of particles in solution. It is also stated that there exists a critical contact angle for this effect, below which the NBS will detach from the surface and lose its role in causing particle aggregation. This is in conflict with the result calculated in Eq. (13), because according to the calculation the convex capillary bridge should play a repulsive role. However, the results of this MD simulation are compatible with the study reported by Sobhy and Tao (2019), which appears controversial. There are differences in the nature of different particles and the values of the critical contact angle vary, and the equations for the calculation of the capillary forces still need further corrections.

The proper use of NBS for flotation recovery of fine particles is a promising flotation technique. However, the mechanism of interaction between NBS and fine/ultrafine particles has not yet been explained. How to obtain high flotation recoveries while ensuring the high stability of NBS is still a challenge for further industrialization of NBS. Optimizing the design of schemes using NBS to recover different types of fine particles is a potential future research direction.

4. Conclusions and prospects

Miniaturization of air bubbles is important for improving the recovery of particulate flotation. Therefore, in order to further improve the sympathy of the direction of this technology's improvement, this paper reviews some of the observations, stability and theoretical doctrines of nanobubbles (NBS), discusses some of the mechanisms by which NBS promotes the efficiency of particulate flotation, and presents the results of the research on NBS in fine particle flotation. Despite the fact that the research on NBS is still partially flawed, it is now shown that NBS flotation has become a promising technological tool for application, and therefore there is still a necessity to gain a deeper understanding of the efficient manufacture and mechanism of NBS's action. By reviewing and discussing the research results of the above staff, the following conclusions and perspectives for the future are drawn:

- NBS has a high stability that is different from that of conventional bubbles, and according to the existing research reports show that the stability of NBS has a correlation with the surface tension

of the solution, temperature, pH, etc., and the current theoretical theory can not be covered comprehensively, and it is necessary to develop an integrated, comprehensive theory to explain.

- The ability of NBS to promote conventional froth flotation and to recover fine/ultrafine particles has been confirmed in reports with potential industrial applications. However, there are still many obstacles to promote NBS flotation technology in industry. One of them is that NBS adsorption on particle surfaces will receive interference from competing adsorption of substances not limited to flotation chemicals, as well as from hydrodynamic influences such as solution flow rate and viscosity in the flotation environment, which need to be further verified for their effects on NBS adsorption. The development of a tailored NBS recovery program that takes into account different types of target particles and equipment will hopefully lead to more efficient recovery of the target minerals.
- The behavior of NBS in improving the recovery of fine particles in flotation may not be limited to the formation of nano-air bridges, lowering the zeta potential of particles, increasing the contact angle of particles, etc. Regarding the enhanced flotation mechanism of NBS still needs to be verified from different perspectives.
- An important part of promoting improved NBS flotation technology in industrial production is the NBS bubble production equipment. The production of NBS in large quantities, with high efficiency and low cost, will largely reduce the obstacles to the promotion of this technology, so the structural improvement of NBS production equipment plays a very important role in the promotion of the industrialization of NBS.
- Develop more accurate nanoparticle identification techniques. Large-scale production of NBS has higher requirements for measurement and identification techniques, and existing measurement techniques are unable to obtain accurate information on bulk NBS. Therefore, future development of sensitive, high resolution, high processing capacity identification techniques is necessary for the accuracy of this technology for production assessment in industry.

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