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# Aqueous dispersions of nanobubbles: Generation, properties and features

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ABSTRACT

Nanobubbles (NBs) have interesting and peculiar properties such as high stability, longevity and high surface area per volume, leading to important applications in mining-metallurgy and environmental areas. NBs are also of interest in interfacial phenomena studies involving long-range hydrophobic attraction, microfluidics, and adsorption at hydrophobic surfaces. However, little data are available on effective generation of concentrated NBs water dispersions and on their physicochemical and interfacial properties. In this work, air was dissolved into water at pH 7 and different pressures, and a flow was depressurized through a needle valve to generate 150–200 nm (mean diameter) NBs and MBs-microbubbles (about 70 μm). Microphotographs of the NBs were taken only in the presence of blue methylene dye as the contrast medium. Main results showed that a high concentration of NBs (number per volume) was obtained by decreasing the saturation pressure and surface tension. The number of NBs, at 2.5 bar, increased from $1.0 \times 10^8$ NB mL$^{-1}$ at 72.5 mN m$^{-1}$ to $1.6 \times 10^9$ NB mL$^{-1}$ at 49 mN m$^{-1}$ (100 mg L$^{-1}$ α-Terpineol). The NBs mean diameter and concentration only slightly varied within 14 days, which demonstrates the high stability of these highly concentrated NBs aqueous dispersions. Finally, after the NBs were attached to the surface of a grain of pyrite (fairly hydrophobic mineral), the NBs dramatically increased the population of MBs, which shows the enhancement of particle hydrophobicity due to NBs adhesion. The results were explained in terms of interfacial phenomena and it is believed that these tiny bubbles, dispersed in water at high concentrations, will lead to cleaner and more sustainable mineral flotation.

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## 1. Introduction

Nanobubbles (NBs[2]) occur as highly stable adsorbed units (interfacial or surface NBs) and spread out as either pancake-like structures or liquid dispersions (bulk NBs). The first report of interfacial NBs is an experimental work that measured the attractive force among hydrophobic surfaces immersed in water (Parker et al., 1994). Accordingly, this behavior is a step-like function of the separation distance among the surfaces, which is ascribed to the presence of submicron bubbles that connect the surfaces. Thereafter, experimental evidence of NBs was provided by Miller et al. (1999), who used Fourier transform infrared (FTIR) spectroscopy to investigate the n-butane-saturated water at a hydrophobic silicon solid. These measurements revealed the accommodation of butane gas by interfacial water at hydrophobic surfaces, supporting the actual presence of NBs.

NBs are gaseous domains that are typically tens to hundreds of nanometers in radius, which are too small to be visible to the naked eye or standard microscopes. Atomic Force Microscope (AFM) images revealed that they form spherical caps, but the precise shape of the NBs remains unclear (An et al., 2015). Today, surface NBs (present in aqueous submerged hydrophobic surfaces) can be detected using different microscopy techniques, most notably tapping-mode AFM (Hampton and Nguyen, 2009; Lou et al., 2000). Chan and Ohl (2012) and Karpitschka et al. (2012) used total internal reflection fluorescence microscopy (TIRFM) for images of hydrophobized glass plate surfaces with adhered NBs.

Bulk NBs are believed to be long-lived gas-containing cavities affected by random Brownian motion. It is now thought that bulk NBs are present in water at room temperature because of the nucleation of stable bubbles. Thus, there is a water affinity property at the nanoscale, whereby the disordered structure of a liquid

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[1] http://www.ufrgs.br/ltm.

[2] In this work, NBs are defined as bubbles that are less than a micron in size (submicron bubbles), although the term "nano" is applied mostly to sizes of approximately 1–100 nm (ISO/TS 27687:2008).

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becomes unstable and results in a spontaneous decrease in local density and formation of nano-sized voids. These voids would serve as nuclei for bubbles that are stabilized by ions (so-called bubstones) (Bunkin et al., 2012). These bulk NBs have been detected using different techniques such as light scattering, resonant mass measurement and a ZetaSizer Nano instrument, which uses Laser Doppler Micro-electrophoresis.

The main properties of NBs are their high stability, longevity and rapid attachment to hydrophobic surfaces. These particularities broaden the potential applications of NBs in many areas such as surface coating and cleaning (Liu and Craig, 2009; Liu et al., 2008; Ushida et al., 2012b; Wu et al., 2008; Yang and Duisterwinkel, 2011), pollutant removal (Agarwal et al., 2011; Fraim and Jakhete, 2015; Kazuyuki et al., 2010; Kerfoot, 2014, 2015; Li et al., 2014; Tasaki et al., 2009; Tsai et al., 2007), energy system improvement (Chan et al., 2015; Hou et al., 2015; Oh et al., 2015; Polman, 2013), medicine (Cavalli et al., 2012, 2013, 2015; Lukianova-Hleb et al., 2012, 2014a,b; Perera et al., 2014), fluidics (Hampton and Nguyen, 2010; Ushida et al., 2012a; Zhang et al., 2006; Zimmerman et al., 2011), and agricultural and acceleration of metabolism in vegetable/animal species (Ebina et al., 2013; Liu et al., 2013; Takahashi and Chiba, 2007).

In the mineral flotation of fine and ultrafine particles, NBs were found to increase the contact angles (coal, phosphates, quartz, and copper minerals), which improves the particle-bubble attachment and decreases the detachment. Other claimed flotation gains are a lower collector and frother dosages required in high kinetic processes (Fan et al., 2012; Sobhy and Tao, 2013a,b; Sobhy, 2013). In addition, in the environmental area, technologies involving NBs have been applied in the removal of amine collector (Calgaroto et al., 2016); bioremediation of groundwater, degradation of surfactants and industrial wastewater treatment (Agarwal et al., 2011; Fraim and Jakhete, 2015; Kazuyuki et al., 2010; Kerfoot, 2014, 2015; Li et al., 2014; Tasaki et al., 2009; Tsai et al., 2007).

Further research involving interfacial and bulk NBs are important to understand the fundamentals and broaden their technological applications. There is a demand for advances in terms of sustainable (workable) generation, mineral particles aggregation, hydrophobizing power and flotation (minerals fines and wastewater treatment and reuse).

In the dissolved air flotation (DAF) process, stable (charged or uncharged) NBs are readily formed after the depressurization of air-saturated water at a high flow velocity, and a known distribution size of NBs can be obtained by either modifying the pH or introducing ionic surfactants (collector-coated NBs). This joint formation of microbubbles (MBs) and NBs was proven notably recently, and a separation technique in which NBs are split from MBs is now available (Calgaroto et al., 2015, 2016).

According to many authors, the extremely high stability and longevity of bulk NBs cannot be explained uniquely by the surface potential and repulsion forces between the bubbles (Craig, 2004; Hampton and Nguyen, 2010; Lima et al., 2008; Ohgaki et al., 2010; Seddon et al., 2011; Weijs and Lohse, 2013). The DLVO theory generally works well under the circumstances for which it was originally intended, i.e., low salt, inert surfaces and interactions at separations greater than a few nanometers. The long-ranged attractions, which are measurable up to several hundred nanometers, among hydrophobic NBs do not fit in this theory. Thus, unfortunately, calculations are difficult to make due to the fact that the forces presumably operate in this size range of the NBs. Further research is required, and many challenges remain (Calgaroto et al., 2014).

This study is a continuation of a series of articles regarding NBs and focuses on their generation as highly loaded aqueous dispersions, characterization, interfacial properties, lifetime and their role in hydrophobizing mineral solids.

## 2. Experimental

### 2.1. Materials

Deionized (DI) water at room temperature (23 °C ± 1) with a conductivity of 3 μS $cm^{-1}$, a surface tension of 72.5 ± 0.1 mN $m^{-1}$ and a natural equilibrium pH of 5.5 was used to produce NBs aqueous dispersions. The DI water was prepared from tap water using a purification system, which consisted of a reverse-osmosis cartridge and modules of ion-exchange resins and activated carbon. A sulfochromic solution and subsequent abundant rinse with DI water were used to remove possible organic compounds from all glass materials. NaCl, which was supplied by Synth® (São Paulo - SP, Brazil) was used to prepare the saline solutions for NBs characterization; NaOH and HCl solutions from Vetec® (Rio de Janeiro - RJ, Brazil) were used for medium pH adjustments.

Methylene blue from Sigma® (St. Louis - MO, USA) was used as a contrast medium to take microphotographs of the NBs.

α-Terpineol (supplied by Química Maragno®; Turvo – SC, Brazil) was used to reduce the water surface tension and NBs generation. This reagent is a 154 g $gmol^{-1}$ molecular weight commercial terpene alcohol with the following molecular formula: $CH_3 - C_6H_9 - (OH) - C_3H_5$.

### 2.2. Methods

#### 2.2.1. NBs aqueous dispersion generation

Bubbles were formed by reducing the pressure of DI water, which was pre-saturated with air at various saturation pressures ($P_{sat}$) during 30 min. This method followed a technique described by Calgaroto et al. (2014), where the supersaturated water was forced through a needle valve (2 mm internal diameter: Globo 012 – Santi®, São Paulo – SP, Brazil), and MBs and NBs were generated in a glass column. The saturation of air in DI water was achieved in a stainless-steel vessel, which contained an internal glass container; the vessel had a height of 15 cm, an inner diameter of 12 cm, and a wall thickness of 1 cm. The container had a height of 14 cm, an inner diameter of 10 cm, a wall thickness of 0.5 cm, and a capacity of 0.7 L.

Then, the MBs were separated from the NBs because the MBs were allowed to rise and escape the glass column (during 5 min), as in Calgaroto et al. (2015). This procedure, which is illustrated in Fig. 1, takes advantages of the high stability of NBs in aqueous systems and their lack of buoyancy (Attard, 2003; Gray-Weale and Beattie, 2009; Hampton and Nguyen, 2010; Ohgaki et al., 2010; Seddon et al., 2011; Weijs and Lohse, 2013).

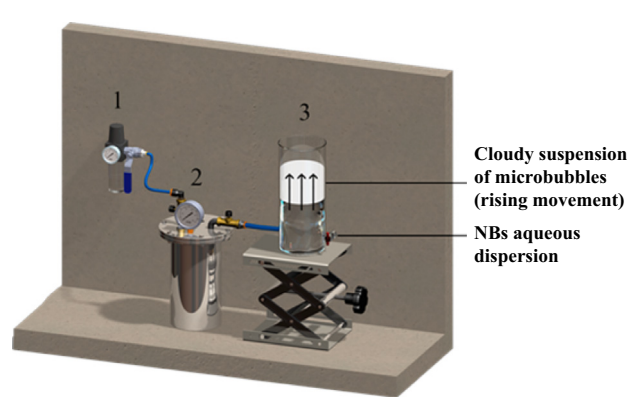


**Fig. 1.** Experimental set-up to generate bubbles and separate the MBs from the NBs. (1) compressed air filter; (2) saturator vessel coupled to a needle valve; (3) glass column.

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