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RESEARCH PROGRESS ON BULK NANOBUBBLES

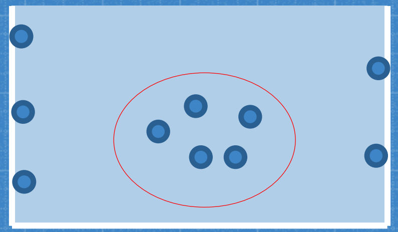
SUMMARY

1. Article’s Motivation
2. Introduction
3. The Discovery of Bulk Nanobubbles
4. Production Methods
5. Characterization
6. Traditional Theory and Bulk Nanobubbles
7. Particle or Bubble?
8. Stability
9. Application
10. Conclusions

Article’s Motivation

- Gather all main discoveries in one place;
- Bring to light the dificulties, limitations and what need to be discovered;
- Point out the importance of nanobubbles;

Introduction



- Bulk and Surface Nanobubbles;
- Much longer lifetime than predicted by Epstein-Plesset Theory;
- It has many characteristics that makes the nanobubble tecnology widely used;
- Can be applied to environmental protection, healthy diet and precise medical treatment.

The Discovery of Bulk Nanobubbles

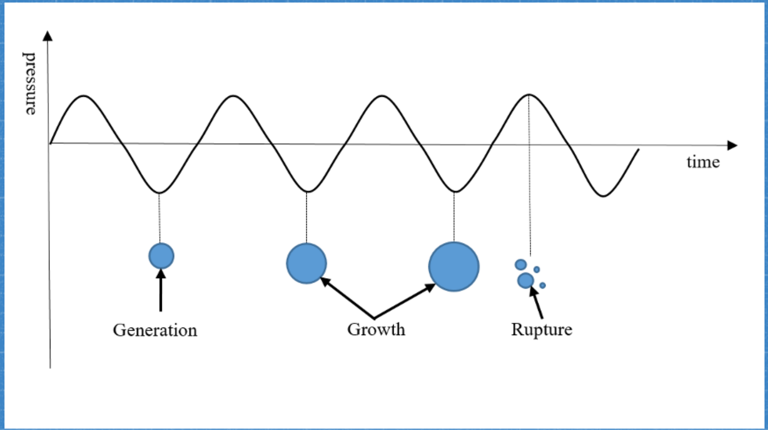
- In 1981, Johnson and Cooke proposed their existence in sea water with lifetime about 22 hours;

- This lifetime was due to natural sulfactants;

- A large number of bubbles forms when the wave breaker in the beach;

Production Methods

- Nanobubbles can be generated by mechanical shear, solution replacement, electrolysis, chemical reaction, turbulence in a Venturi tube, ultrasonic cavitation, dissolved gas release, heating, flow through porous materials,etc. And combining them;



Production Methods

- **Ultrasonic Technique**: The pressure of liquid will change because of the vibration of sound wave, and the cavitation nucleus will be produced because of the shear action of fluid or the supersaturation of the dissolved gas in the local area;

- **Mechanical Shear**: Large bubbles first form due to supersatured solution. It will be destroied by high speed rotating impellers or gears forming bulk nanobubbles;

- **Electrolysis**: Oxygen is produced near the anode and hydrogen near the cathode making the solution supersatured;

Production Methods

- **Atmospheric decompression**: Based on Henry's law, after a depressurization part of the gas will evolve into nanobubbles in the supersaturated solution;

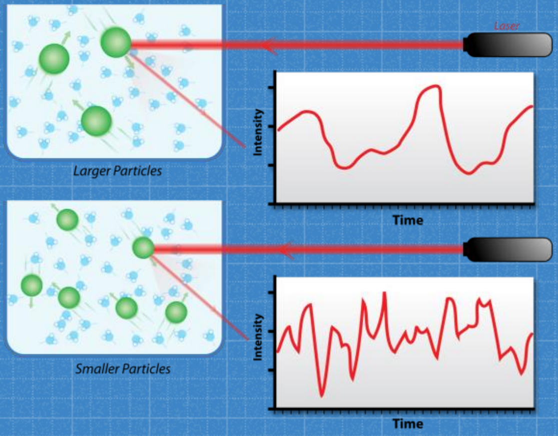
- **Solution substitution**: Today is the most common Method. Requires two solutions with different solubility and one can dissolves entirely the another. When the substitution takes place, the excessive gas naturally forms nanobubbles.

Characterization

- A bulk nanobubble involves measuring hydraulic diameter, concentration and size distribution;
- Its uncertain if Laplace pressure theory is applicable since its hard to measure gas density and pressure inside of them;
- Here they discuss the Dynamic Light Scattering (DLS), Nanoparticle tracking analysis (NTA), Resonance mass measurement, Rapid freezing and electric induction Method.

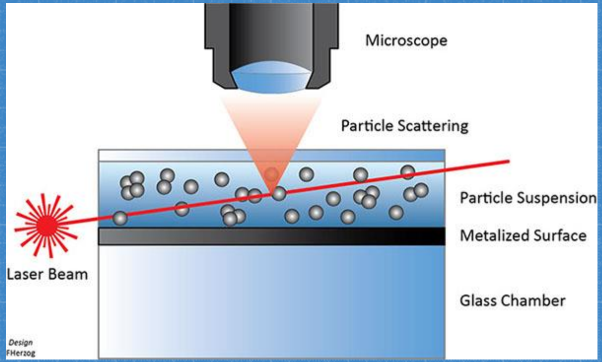
Characterization

Dynamic Light Scattering (DLS)



Radius can be measured from Einstein equation of Brownian Motion;

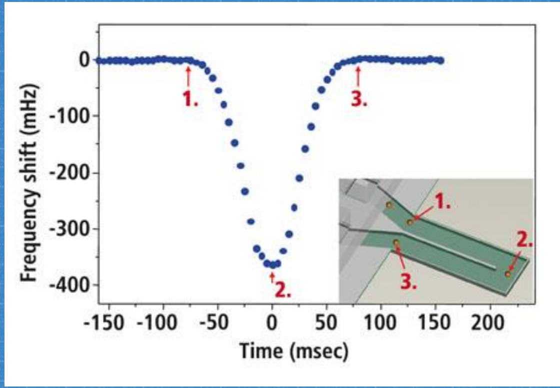
Nanoparticle tracking analysis (NTA)



Simultaneously measure the concentration and size distribution of particles;

Characterization

Ressonance Mass Measurement



Measure density, so its possible to distingues between nanobubbles and solid particles;

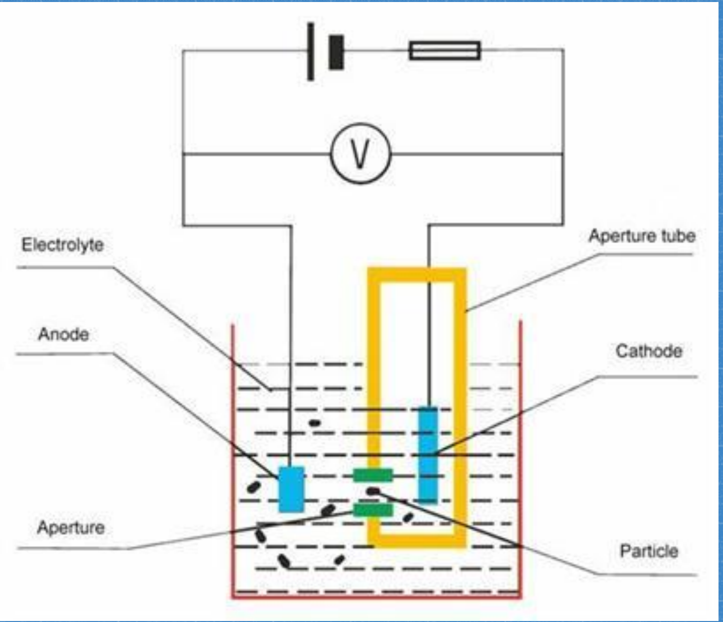
Rapid Freezing

Its possible to obtain the number of nanobubbles indirectly;

Characterization

Electric Induction

The impedance change is proportional to the volume of particles passing through the channel, so the device can also be related to the number and size of bubbles flowing through the channel.



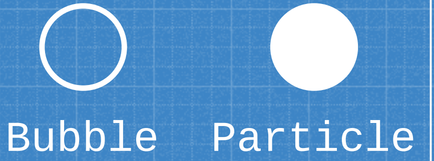
Traditional Theory and Bulk Nanobubbles

- In 1950, Epstein and Plesset developed a theory of gas diffusion in bubbles;
  - Around the bubble: Henry’s law
  - Away from the bubble: Quantity of dissolved gas

- Bubble lifetime with the diameter bigger than 1μm is predicted with experimental confirmation;
  - Bubble’s lifetime with diameter ≤ 1μm being 0.02sec

- There is some experiments have reported the existence of bulk nanobubbles from hours to weeks;

Particle or Bubble?



- In experiments, contaminants may be introduced unintentionally;

- That was seen when degassing a solution the light scattering didn’t desappeared;

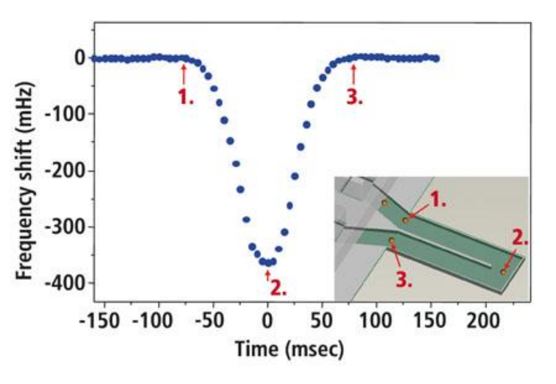
- Some nanoparticles seems to be gas aggregates:
  1. Shrinks under positive pressure and grows with negative Pressure;
  2. The density is lower than the density solution;
  3. Zeta potential is consistent with larges bubbles;
  4. Refractive index lower than the solution.

Particle or Bubble?

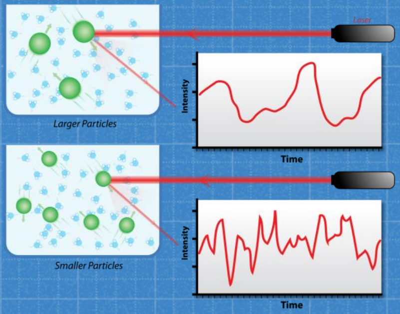
Alheshibri and Craig used pressure dissolution and depressurization to produce bulk nanobubbles. The density and compressibility of nanoparticles can be used to distinguish nanoparticles from nanobubbles.

They found that the density of the nanoparticles was less than, but very close to, the density of water.

When the applied high pressure, the change of the diameter of nanoparticles is almost zero. The results show that these particles are nanoparticles, not nanobubbles.



Resonance Mass Measurements



Dynamic Light Scattering

Particle or Bubble?

Rak et al. investigated the role of ultrasonic cavitation in the production of bulk nanobubbles.

Measuring the density of the nanoparticles with a incremental centrifuge. It turned out to be much higher than the density of the solution. So these nanoparticles are definitely not nanobubbles.

The nanoparticles in the solution were confirmed to be solid nanoparticles of titanium and vanadium from the ultrasonic probe.

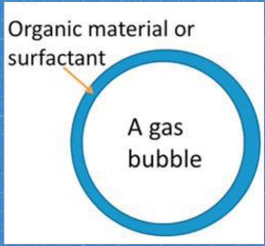
Particle or Bubble?

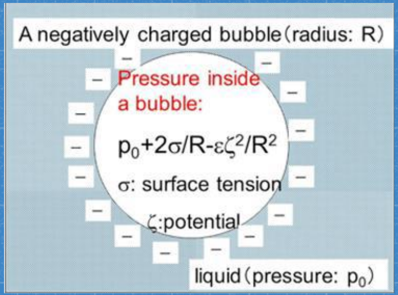
- Some pollutants have been mistaken as bulk nanobubbles, which objectively raises or strengthens researchers' doubts about the Epstein-Plesset theory;
- There is no widely accepted method to determine nanobubbles, nanoparticles or any other thing when they have a density close to the bulk liquid density;
- Need to combine multiple conditions to verify the results;
  - Volume change
  - Density
  - Zeta potential
  - Refractive index
- The authors point out that a better understanding of interface theory will help researchers to distinguish them.

Stability

- Yasui et al. explored several stabilization models for bulk nanobubbles:

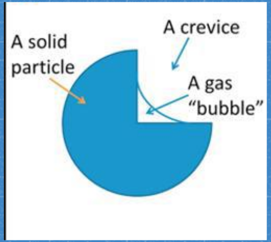
Skin Model

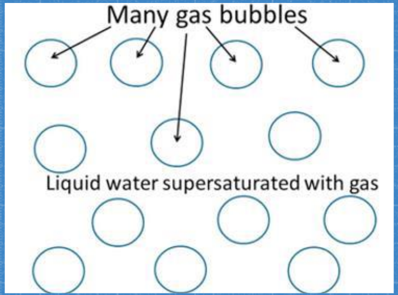




Electrostatic Repulsion Model

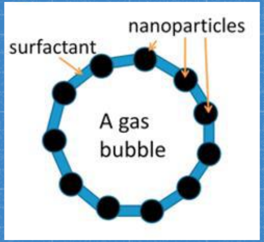
Particle Crevice Model





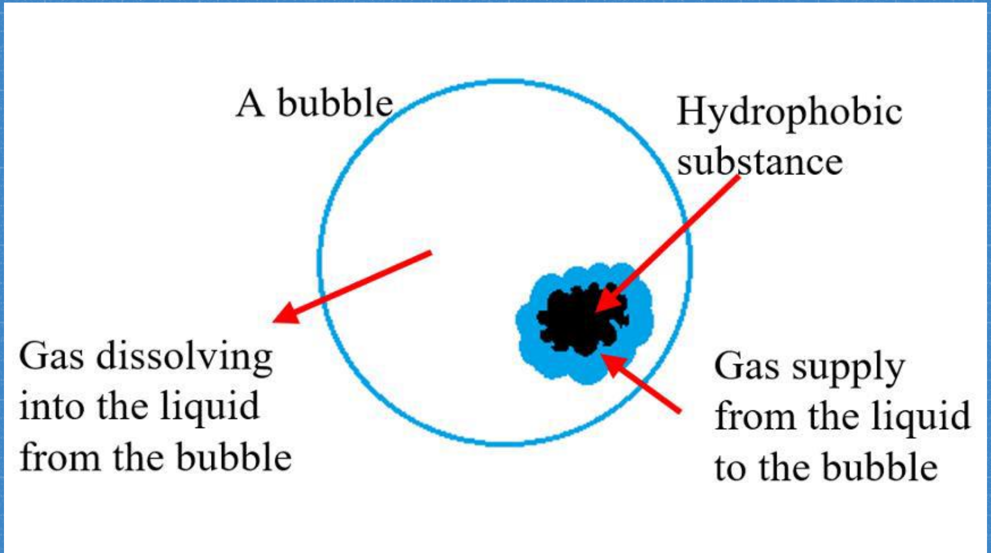
Many Body Model

"Armormed" Bubble Model



Stability

- Yasui et al. have developed a dynamic equilibrium model of bulk nanobubbles based on the relevant model of surface nanobubbles:



Stability

- Another stability conditions is proposed by other authors:
  - Changes in surface tension caused by changes in bubble size plus adsorption of pollutants pushes to equilibrium;
  - Small amounts of etanol in water solution can provide a stable lifetime of 3 months;
  - Existence of negative ions in interface that reduces surface tension and make them stable;

Stability

- They have high Zeta potential, which guarantee electrostatic repulsion and avoid coalescence;

- Presence of solid particles improves stability since there is more nucleation centers;

- Bulk nanobubbles lasted longest and maintained a highest concentration in alkaline solution relatively;

Applications

- Importants characteristics: long lifetime, high specfic surface area, surface charge;

- **Wastewater treatment**: Bulk nanobubble can extract poluents, adsorving nanoparticles trought collision or bubble nucleation. They combine to form larger aggregate and finally solid-liquid separation;

- **Surface Cleaning**: Due to high surface area and surface charge they can adsorb and remove contaminants from solid surfaces (protein from surface,reverse osmosis membranes, etc). Their use reduces water consumption and use of additive/detergents;

Applications

- **Promoting Growth of Animals and Plants**: Hydroxyl radical (-OH) and superoxide ion (-O_2-) can be produced with bulk nanobubbles, which promotes growth of plants and animals. And, due to high gas-liquid mass transfer efficiency, the dissolvend oxygen content can be increased and last longer improving the water quality to raise sea food (fish, shrimp);

- **Medical Examination and Treatment**: Micro drugs agents can't pass through blood vessels, what nano drugs agents surely do. It can reach the interior tissue to realize local treatment with less damage to entire body since the dosage is reduced. Besides that, oxygen-enriched water can improve life for people in high altitude.

Conclusions

- The ultra-long stability of bulk nanobubbles is still a worldwide mystery;
- Because nanobubbles are close in size to the limit of the continuum model of fluid, and involve the complex flow of gas-liquid-solid multiphase coexistence, it is of great scientific significance to examine in detail whether the governing law still accords with the traditional theory;
- With the development of the theory of bulk nanobubbles and the growing demand of industrial applications, basic research and technique development on bulk nanobubbles are expected to boom in the near future.

THANK YOU!

1950	1981	2010	2014	2016	2018	2019
The theory of bubble dissolution and growth (Epstein & Plesset, 1950)	Johnson and Cooke firstly proposed the existence of bulk nanobubbles (Johnson & Cooke, 1981)	Nanobubbles were imaged by cryo-scanning electron microscopy (Ohgaki et al., 2010)	The Zeta potential of nanobubbles was obtained for the first time (Calgaroto et al., 2014) The density of bulk nanobubbles was measured (Kobayashi et al., 2014)	The photo of the bulk nanobubbles was obtained by optical microscope (Azevedo et al., 2016)	The density of nanoparticles that are considered as nanobubbles is $0.95 \pm 0.07 g/cm^3$ (Alheshibri & Craig, 2018)	The so-called nanobubbles produced by ultrasonic cavitation and alcohol-water replacement are metal nanoparticles and hydrophobic organic pollutants (Rak et al., 2019; Rak & Sedlak, 2019)