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A Henry's law method for generating bulk nanobubbles

by

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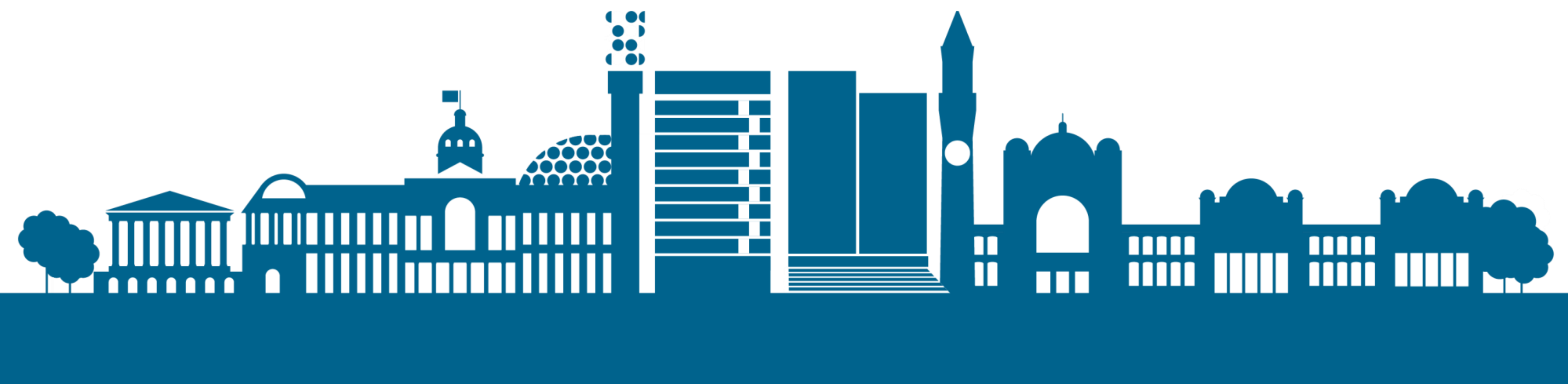


Outline

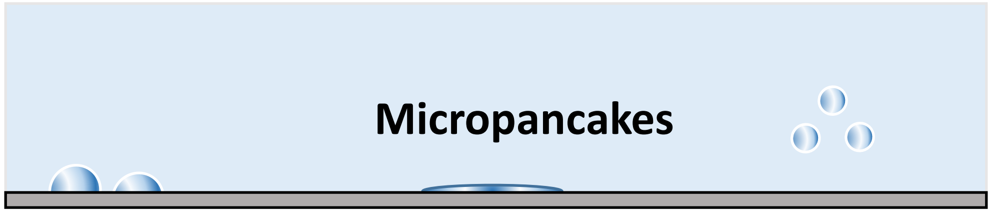
- **Introduction**
- **Characterisation techniques:**

  - Dynamic Light Scattering (DLS)

  - Nanoparticle Tracking Analysis (NTA)
- **Generation method**
- **Results**
- **Conclusions**

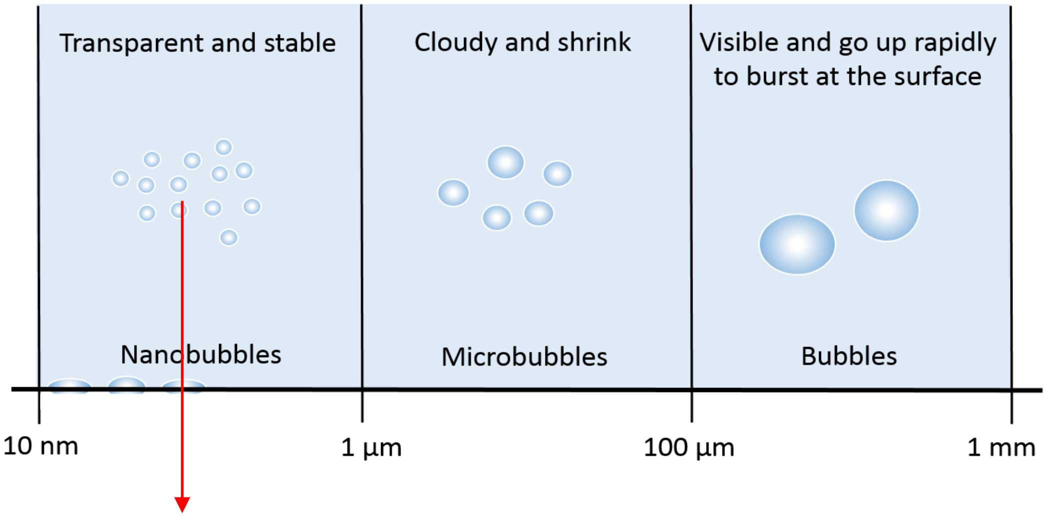
Introduction

What are Nanobubbles?



Surface Nanobubbles (SNBs)

Bulk Nanobubbles (BNBs) or Ultrafine Bubbles (UFBs)



Observed in the range between 60 – 200 nm

- Epstein and Plesset (1950)
- Ljunggren and Eriksson (1997)

Gas-filled bubbles (10-100 nm in size) have a short lifetime (1-100 µs)

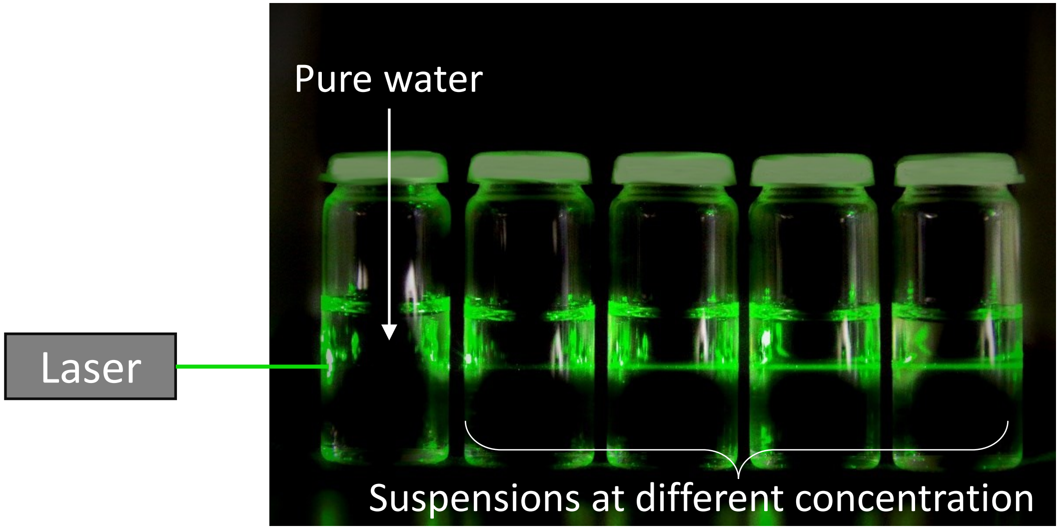
Nanobubbles show a long term stability (days/months)

Nanobubbles or Nanoparticles?

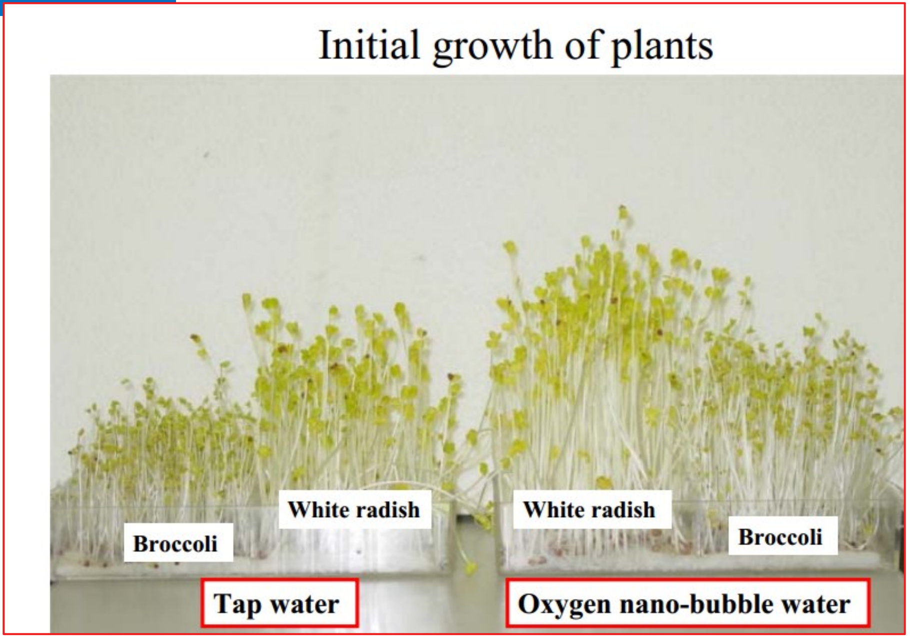
- **Difficulties to make a distinction between solid nanoparticles and gas filled nanobubbles**
- **Easy to generate contamination in the nanoscale**
- **Lack of instruments to make that distinction**

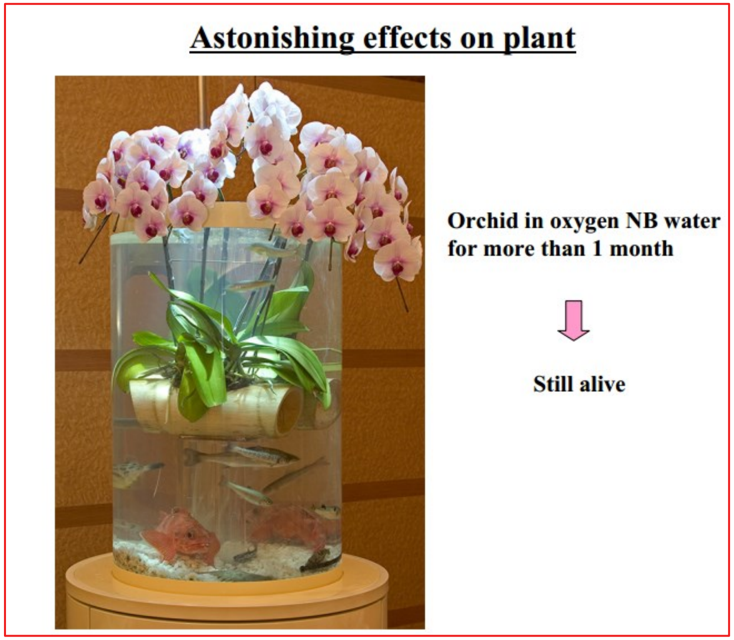
Bulk Nanobubbles properties:

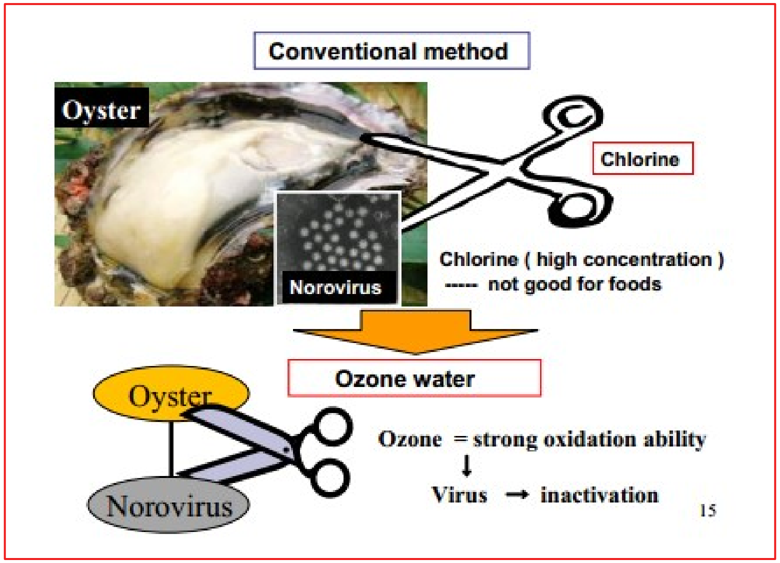
- **Negatively charged**
- **Scatters light**
- **High volume to surface ratio**
- **Could be stable for several months**



Wide range of applications







...but also for **surface cleaning** reducing amount of detergents;

...reduction of **fuel** consumption and poisonous exhaust gases if added in fuel;

...**food** industry;

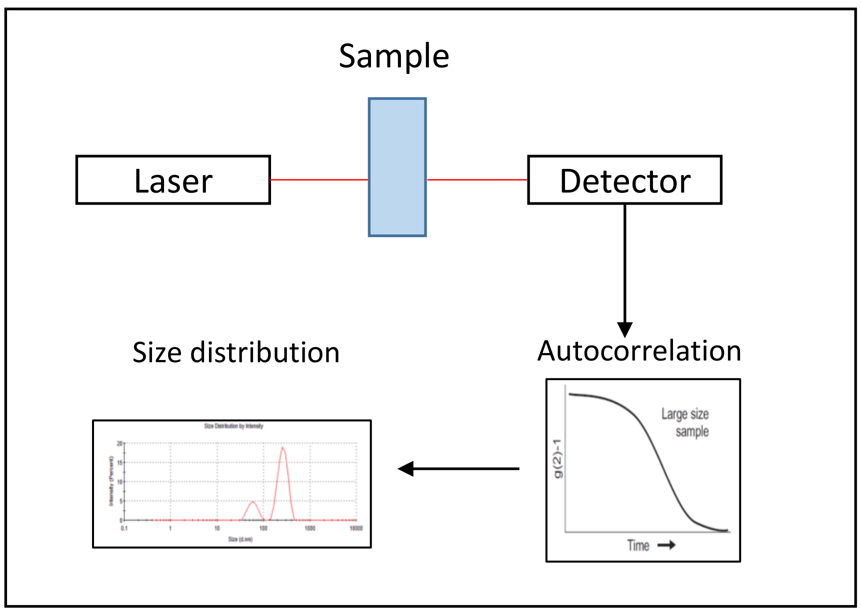
...**ultrasound contrast agents** for diagnosis and as drug carriers for therapy;

...**wastewater treatment** (used in lakes and rivers).

Pictures from Masayoshi Takahashi

Dynamic Light Scattering (DLS)

- **Light Scattering**
- **Brownian Motion**
- **The size distribution is intensity-weighted**
- **Overestimation of the width of the peaks in the distribution**
- **Zeta potential can also be measured**



Schematic diagram of DLS

Autocorrelation function

Where:

I = intensity
t = time
τ = delay time

$$G(\tau) = \left\langle \frac{I(t_0) * I(t_0 + \tau)}{I(t_\infty)^2} \right\rangle$$

can be modelled with

$$G(\tau) = \mathrm{B} + A \sum e^{-2q^2 D\tau}$$

Where:

B = baseline at infinite time
A = amplitude
q = scattering vector = $(4\pi n/\lambda_0)\sin(\theta/2)$
n = dispersant refractive index
λ_0 = laser wavelength
θ = detection angle
D = diffusion coefficient
τ = correlator delay time

Stokes-Einstein equation

$$D = \frac{K_B T}{3\pi\eta d_H}$$

Where:

d_H = hydrodynamic diameter
k = Boltzmann's constant
T = absolute temperature
η = viscosity
D = diffusion coefficient

Nanoparticle Tracking Analysis (NTA)

- **Light Scattering**
- **Brownian Motion**
- **Optical microscope**
- **The Three-dimensional movement is tracked only in two dimension**
- **It is possible to determine D from measuring the mean squared displacement of a particle in one, two or three dimensions.**

Stokes-Einstein equation

$$D = \frac{K_B T}{3\pi\eta d_H}$$

Where:

d_H = hydrodynamic diameter
K_B = Boltzmann's constant
T = absolute temperature
η = viscosity
D = diffusion coefficient

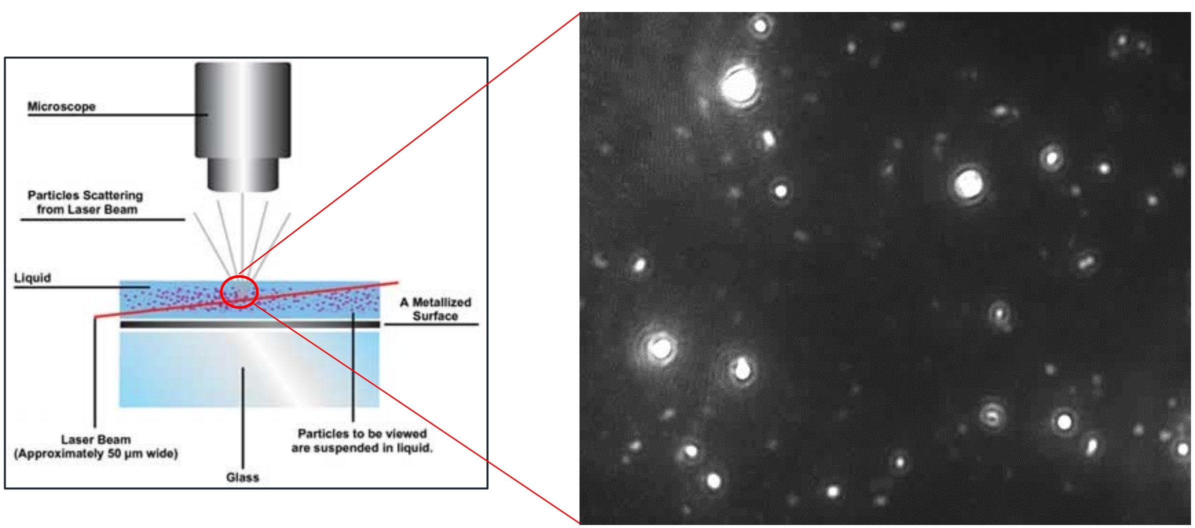
$$\overline{(x^2)} = \frac{2TK_B t}{3\pi\eta d}$$

$$\boxed{\overline{(x,y)^2} = \frac{4TK_B t}{3\pi\eta d}}$$

$$\overline{(x,y,z)^2} = \frac{2TK_B t}{\pi\eta d}$$

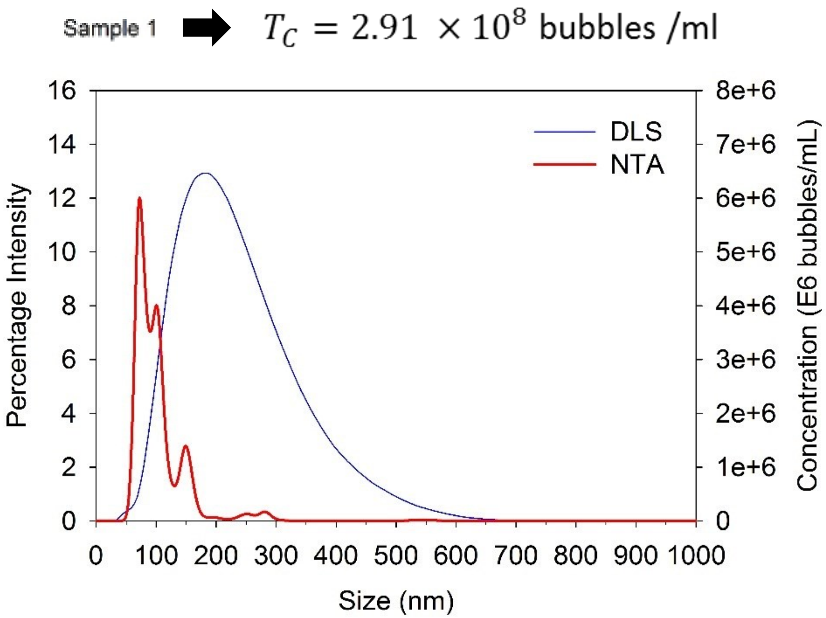
Where:

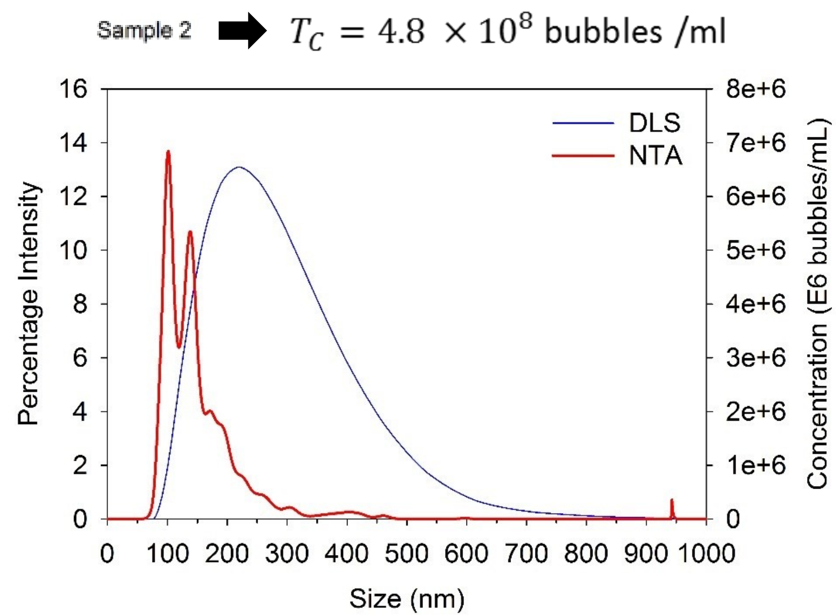
$\overline{(x^2)}$, $\overline{(x,y)^2}$, $\overline{(x,y,z)^2}$ = mean square displacements in one, two and three dimensions respectively



Schematic of NanoSight principle (Malvern Panalytical)

DLS vs NTA





Bubble size distribution by Dynamic light scattering (DLS) and Nanoparticle tracking analysis (NTA)

- **NTA provides a number weighted distribution**
- **DLS provides an intensity weighted distribution**
- **DLS makes an overestimation of the size distribution**

Smaller bubbles are ‘over-shadowed’ and not detected if the sample contains so much scattering signal from the larger species

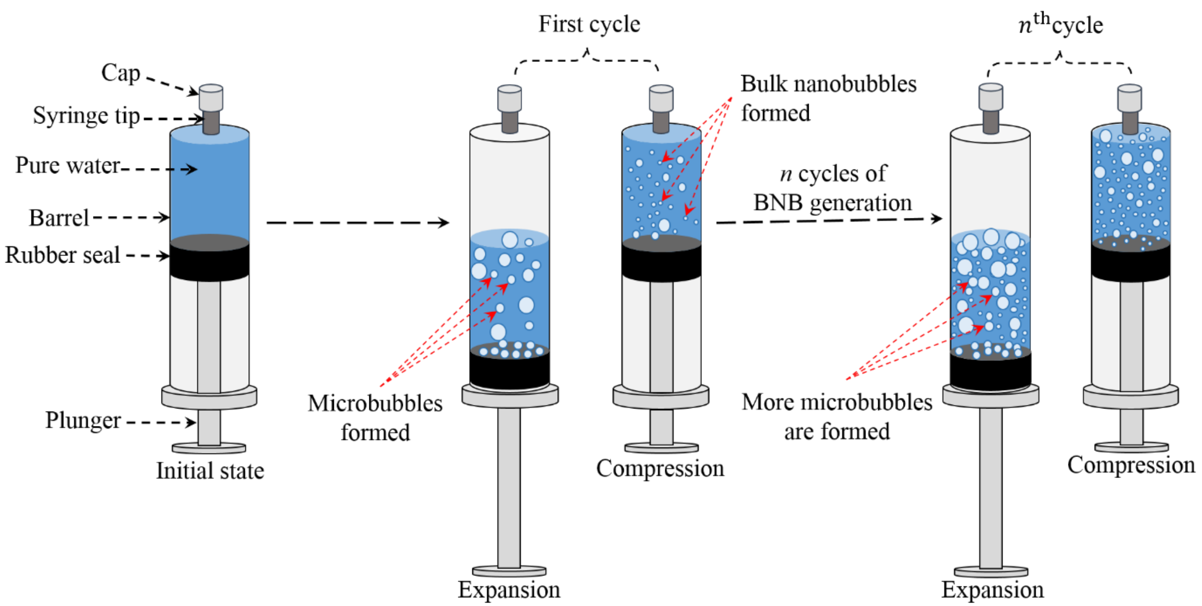
Generation method

- **According to Henry's law, at constant temperature, the saturation concentration of gas in a given liquid, *i.e.* the amount of dissolved gas, is directly proportional to the partial pressure of the gas above the liquid, thus:**

$$C = H \times P_{\mathrm{g}}$$

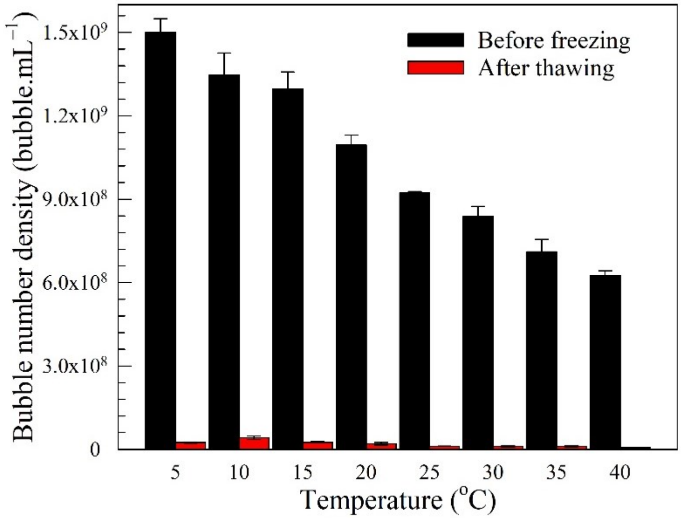
where, *C* is the gas solubility at a given temperature in a particular solvent, P_{g} is the partial pressure of gas and *H* is Henry's law constant

- **subjecting the liquid to reduced pressure makes the dissolved gas less soluble and, hence, leads to gas molecules being released**

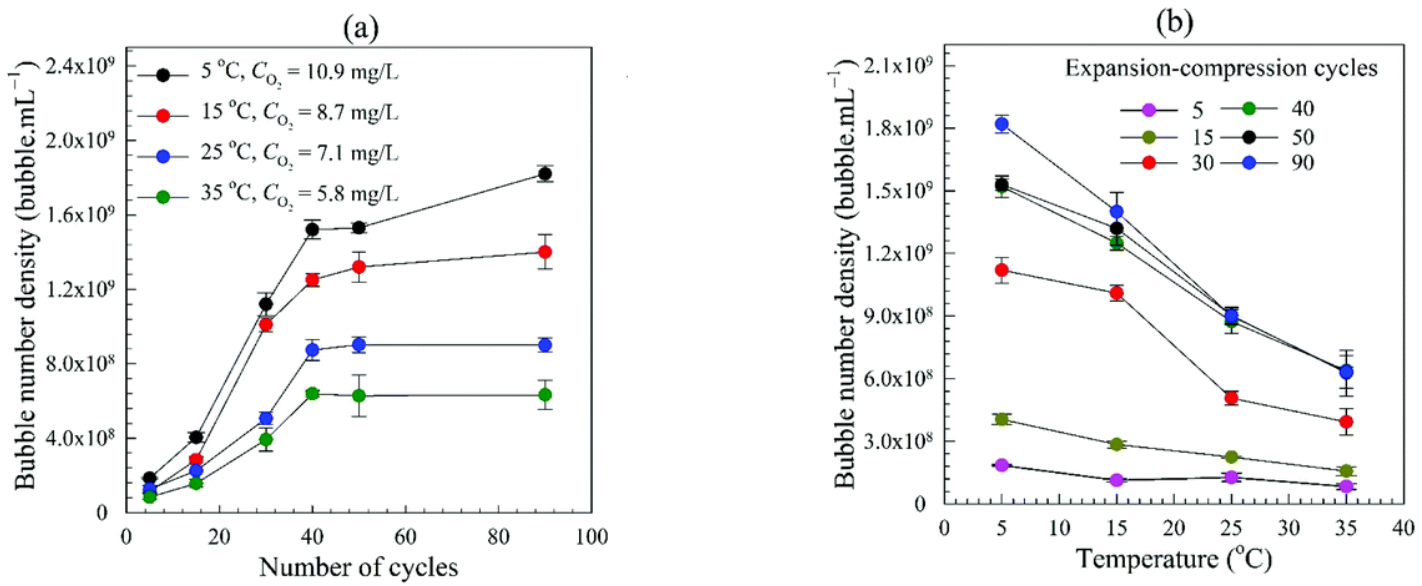


Results – Proof of existence

- **Nanobubbles disappearing of > 96% after freezing-thawing**

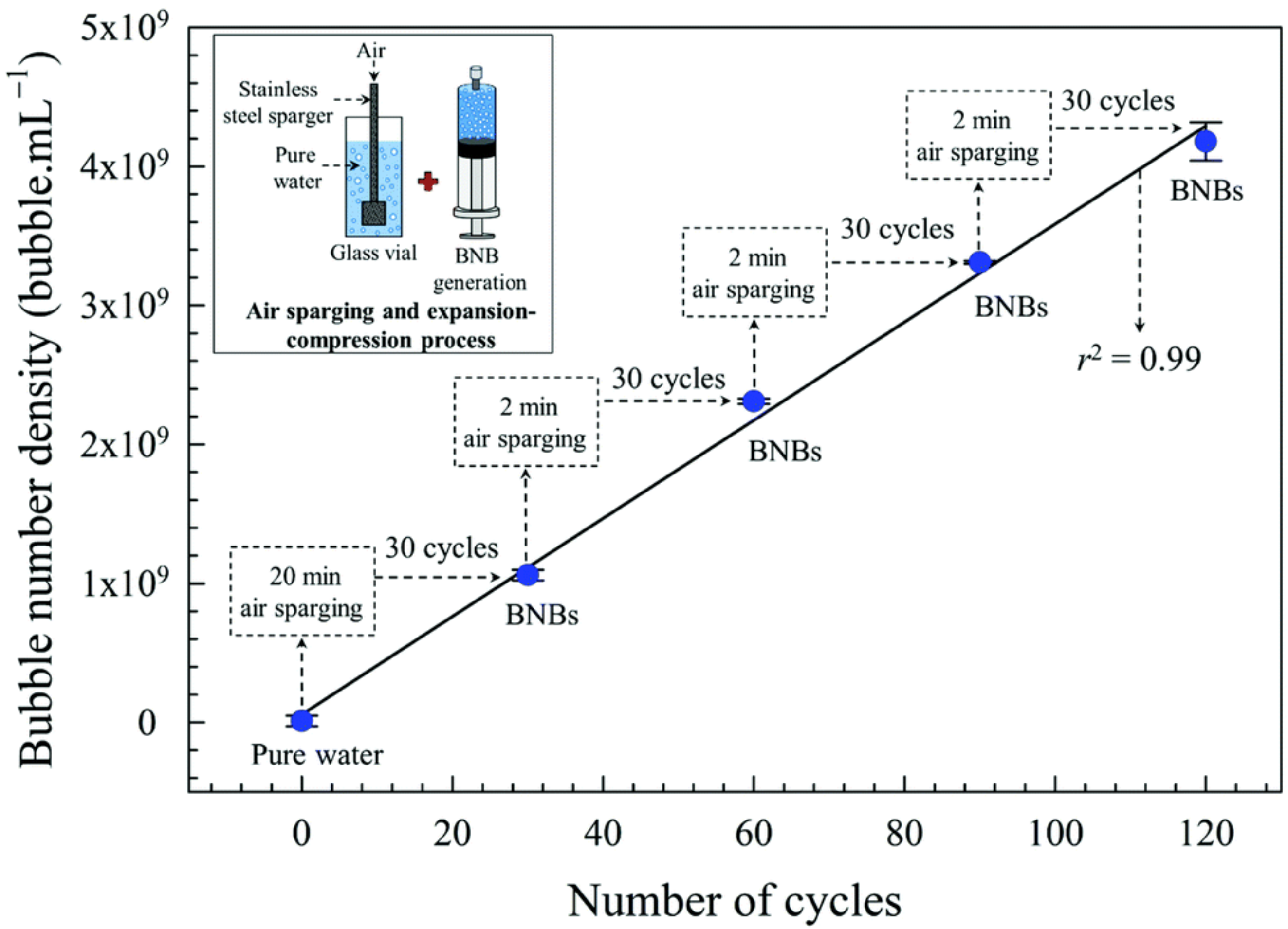


- **Effects of air solubility: more bulk nanobubbles are produced at lower temperature**



Results – Proof of existence

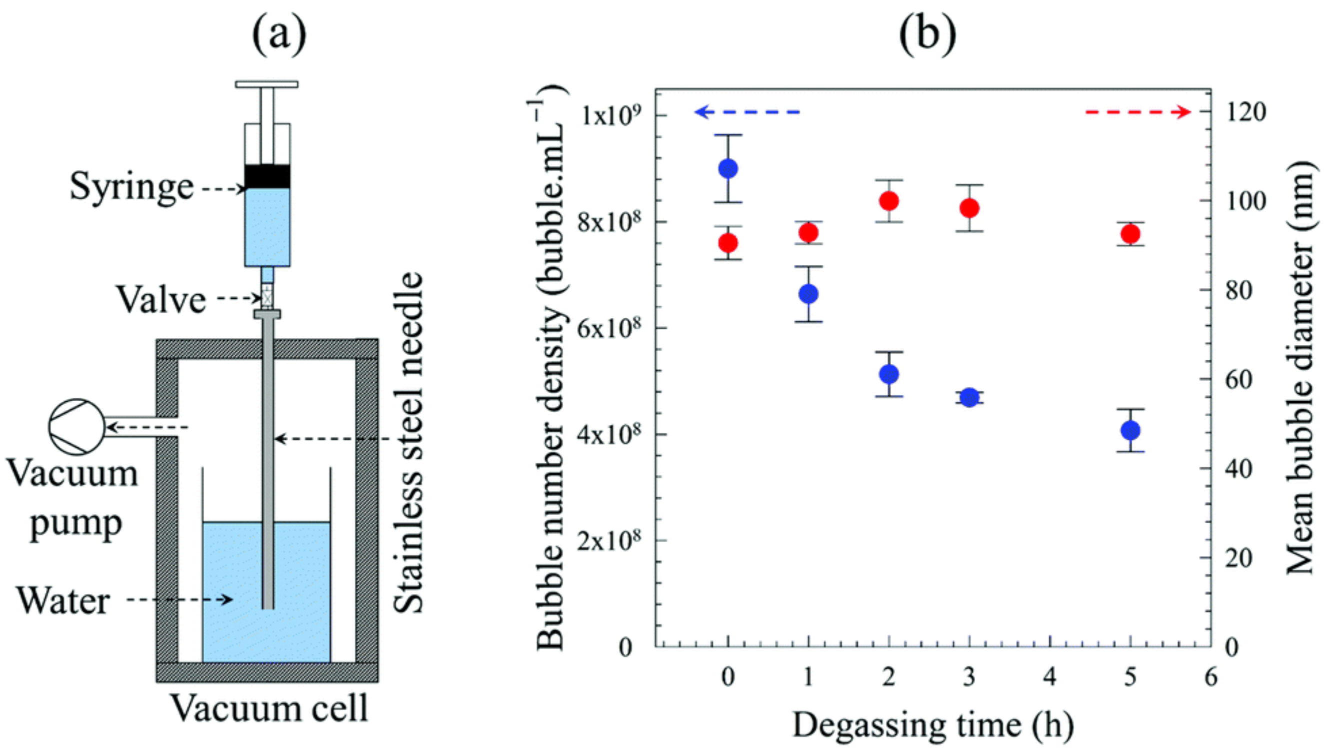
- **Effect of air sparging: repeated sparging of air might provide a mechanism for producing significantly higher concentration of BNBs.**



Results – Proof of existence

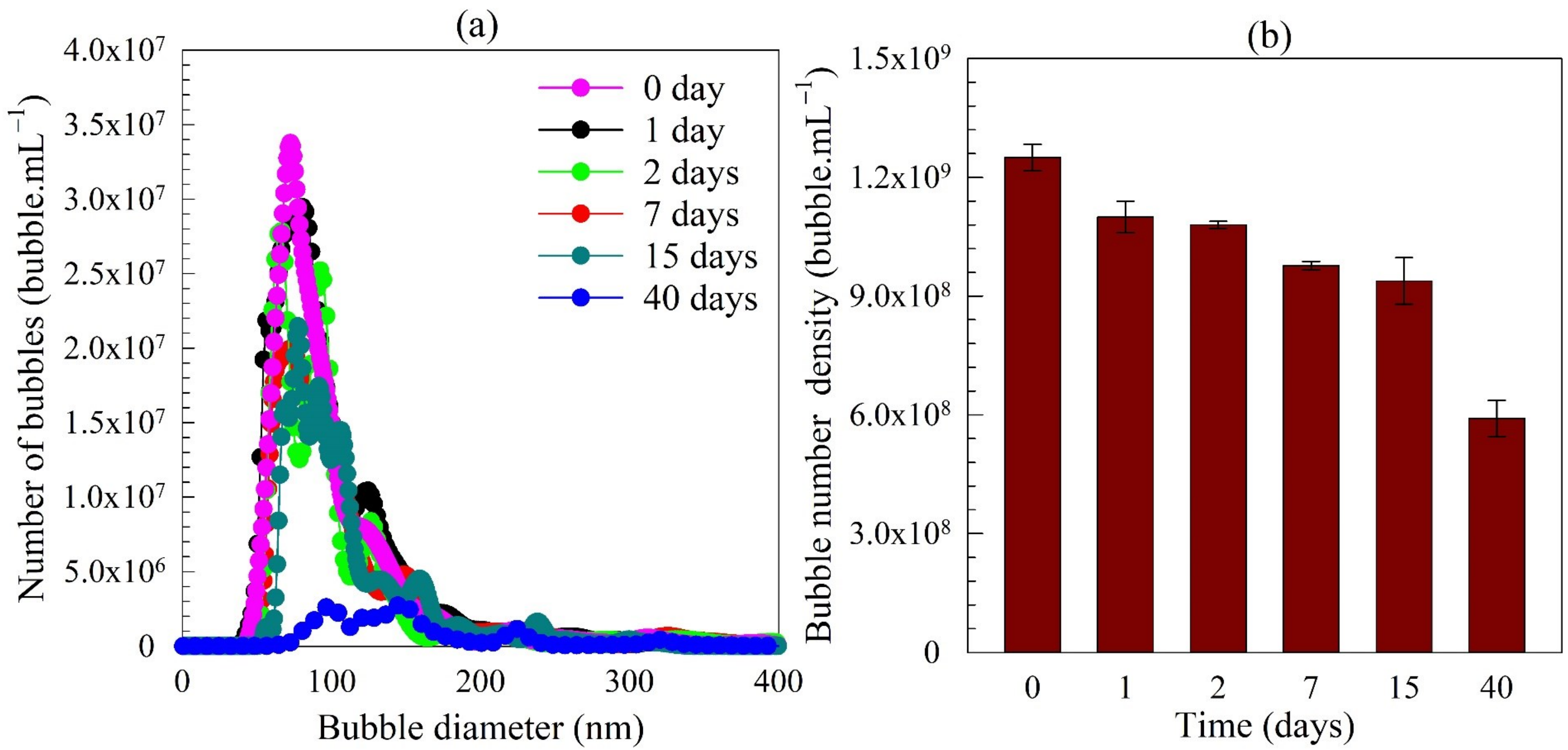
- **Effect of water degassing: pure water had been partially degassed at 15 mbar.**

- **The longer the water degassing time, *i.e.* the less the dissolved air content, the fewer the nano-entities observed per unit volume. After a degassing time of 5 h, there is about 50% reduction in the number density of nano-entities generated compared to undegassed water.**



Results – Long term stability

- **Gradual disappearance of Bulk Nanobubbles over time**
- **On the basis of these observations, we can safely discount the possibility of solid nanoparticles disappearing through growth in size by aggregation (constant mean diameter) and sedimentation (samples were stirred before NTA analysis). The gradual depletion of nano-entities over time, therefore, supports the hypothesis that they are gas-filled bubbles.**

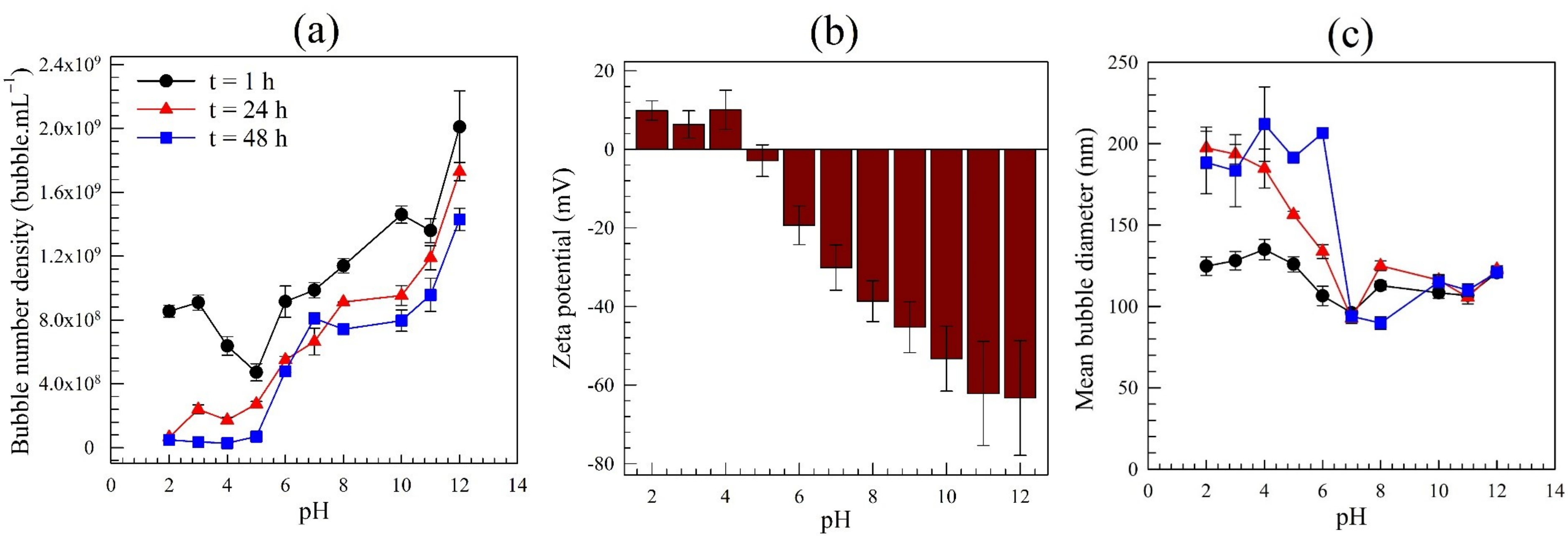


Results – Effect of pH on BNBs stability

- Effect of water pH pre-adjusted in the range 2-12 by addition of HCl to make acidic solution and KOH to make basic solutions.

- The bubble number density increases sharply as a function of pH. A large number density can be achieved in acidic solutions but they are relatively shorted-lived compared to the bubbles generated in basic solutions.

- A plausible reason for the relatively weak stability of BNBs in acidic solutions is a shortage in hydroxyl ions which normally attach to bubble interfaces to stabilise them.



Conclusions

- **The technique based on Henry's law's principle of vacuum degasification has been developed to generate concentrations in excess of 10^9 bubble/mL of stable bulk nanobubbles in pure water**

- **The number of bubbles generated increases as a function of the number of expansion–compression cycles up to a point and then levels off as the available dissolved gas is depleted**

- **Added sparging of gas enhances their number density**

- **They showed a long-term stability (up to several weeks) gradually disappearing over time whilst their mean size remains unchanged**

- **The charged nanobubble interface is postulated to create an external negative electrostatic pressure which balances the internal Laplace pressure so that, at equilibrium, no net gas diffusion occurs**

- **BNBs enjoy much higher stability in alkaline solutions than acidic ones**

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Thank you