Massive generation of metastable bulk nanobubbles in water by external electric fields
8 April 2020, by Thamarasee Jeewandara

Schematic of pressure vessel rig. (A) The four main sections are gas supplier, distribution terminal, the pressure cell itself, and temperature regulation jacket. High-purity (N5-level) gases (methane and O2) are supplied to the 0.34-liter, 200-bar–rated stainless steel and rocker-mounted vessel through the distribution terminal, with line cleaning before purging the desired gas, by way of a mass flow controller and accurate measurement of gas loading into the deionized water-loaded vessel. The system operates under constant volume modes, with the inlet valve closed upon reaching the desired pressure (~90 bar), and pressure logged digitally every second for the experiment’s duration. A temperature control system operates in a jacket around the vessel (held at 20°C). A 60-V DC electric current supply was introduced via sheath-covered wires (preventing direct wire-water contact) into a three-dimensional–printed plastic (B), horizontally mounted holder immersed in water. (Photo credit: Mohammad Reza Ghaani.) Credit: Science Advances, doi: 10.1126/sciadv.aaz0094

Nanobubbles are nanoscopic gaseous forms that can exist on solid surfaces or in bulk liquids. Bulk NBs can be present in most aqueous solutions due to constant agitation and cosmic radiation—attracting significant attention for applications in nanoscopic cleaning, to control boundary slip in microfluidics, wastewater treatment, heterocoagulation and medicine. Scientists credit the long-lived presence of NB’s to negative-charge build-up at the bubble/liquid interface and a strong electron affinity at the surface. Independent of the NB diameter, the mutual repulsion between NBs in water are large enough to prevent coalescence and slow the rise of buoyancy. Scientists can regulate the size of NBs in the presence of surface-active agents and use resulting coated bubbles as ultrasound contrast agents or for targeted drug delivery.

In this work, Ghaani et al. tackled fundamental factors governing the NB’s pH-, ionic- and magnetic field-sensitive nature, including surface electrostatics. They aimed to determine if externally applied electric fields could manipulate, dictate, control and enhance NB formation. If such external
forces had an effect, they investigated their energy cost and electro-induced alterations. When the team applied low electric energy, they observed massive and rapid enhancement of metastable NB gas accommodation in water. The scientists investigated if the first-in-study results for NB generation occurred in the bulk liquid or at the liquid interface and identified the phenomenon to be due to bulk NBs using a bulk-probing NB detection/diagnostic tool.

Gas uptake as a function of time. Results shown for oxygen (A) and methane (B) at 60 V (with average field intensity of 12 kV/m), expressed as a multiple of their respective HLCs (right axis) and in g/liter (left axis) at prevailing background pressures of ~90 bar; plateaux occurred within less than 3 hours. Credit: Science Advances, doi: 10.1126/sciadv.aaz0094

The team initially placed deionized water in a pressure vessel and fed pure gas to ~90 bar, closed the vessel and regulated the system's temperature. When the setup reached Henry's Law gas-solubility level within two hours, they activated an external sustained static electric field inside the liquid water using a 60 V direct current (DC) source. Within three hours or less, they achieved greatly elevated gas uptake plateau in the water and noted a flux of gas molecules form the bulk gas phase in the liquid during NB formation, causing the pressure to drop. Comparatively, the energy required to form NBs using electric fields were extremely low and pointed to extraordinarily high levels of energy efficiency.

For example, the energy required to form NBs equalled 0.3 W hour/m³; much lower than that in advanced systems such as wastewater industries (~40 W hour/m³). Furthermore, while wastewater aeration typically allowed ~1 to 2 mg/liter of dissolved oxygen, the team achieved ~25 to 35 mg/liter of dissolved oxygen with NBs that were metastable for months. Using nonequilibrium molecular dynamics (NEMD) Ghaani et al. then explored the underlying molecular mechanisms behind the startling gas accommodation increase observed experimentally in water. It appeared that the more hydrophobic the gas, the more accentuated the electric field effect to amplify the massive increase in the capability to form bulk NBs. The results also suggested that NB formation maybe kinetically dominated.

NB formation and ensuing stability enhancement via applied static electric fields in NEMD. (A) Starting with individually solvated propane molecules in water (top), field application leads to NB formation: The bottom panel shows NBs within 3 ns in a field (1.5 V/nm). (B) Evolution of the accessible bubble surface area to water molecules; increasing NB stability is evident—1.5 V/nm readily promotes NB formation, with a higher surface area, stable for more than 10 ns. Credit: Science Advances, doi: 10.1126/sciadv.aaz0094

The team next ran NEMD (nonequilibrium molecular dynamics) simulations for both propane and methane in water and observed similar results for both gases. During the simulation, Ghaani et al. applied external fields of much greater intensity than those used for the experiments to observe credible results with minimal signal-to-noise ratio, for more than million-atom NEMD, spanning tens of nanoseconds. The more intense fields promoted NB formation readily with higher surface area in the simulation.
Since the long-lived NB stability is well known, the team studied the metastability of NBs after field removal and exposure to ambient pressure. To understand if NBs are localized at the surface or distributed in bulk, the team used dispersive light scattering (DLS) as a bulk probing method and detected NBs throughout the bulk liquid. However, the scientists also noted unusually transient micro-to-macro-sized bubbles at the polytetrafluoroethylene (PTFE) surface in the system born of nano- to micron-scale bubble nucleation after applying an electric field. Ghaani et al. observed the excess oxygen water/gas localized bubbles to destabilize mechanically within six hours, while limited bulk-bubble loss occurred after six to 50 hours. After a period of four months, the remaining NBs enlarged in size as measured with DLS (dispersive light scattering).


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