

Ultrahigh density inside a nanobubble

HaiPing Fang^{1,2*}

¹ Department of Physics, East China University of Science and Technology, Shanghai 200237, China;

² Zhangjiang Laboratory, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

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Gas bubbles are very common in our daily life and are often seen in water and beer. For a large gas bubble in a liquid, the pressure difference ΔP within and outside the bubble is governed by the Laplace equation $\Delta P = \gamma/R$, where γ is the surface tension at the interface between the bubble and liquid, and R is the bubble radius. Clearly, for tiny bubbles, inner gas pressure will be very high; thus, the bubbles will be unstable and rapidly dissolve in water. For example, a bubble with a radius of 10 nm will have the inner pressure of 1.459×10^7 Pa [1]. Surprisingly, in 2000, Lou et al. [2] have reported their direct experimental observation of bubbles at the nanometer level (named as nanobubbles) on hydrophobic graphite or hydrophilic mica surfaces in water by atomic force microscopy. Those nanobubbles were stable overnight and for several days. Later, nanobubbles have been widely observed on various surfaces and even in bulk water and have attracted great attention [3]. Currently, a series of international conferences focused on nanobubbles and their applications have been founded. There are wide applications based on nanobubbles, such as wastewater recovering, aquaculture, agricultural planting, surface cleaning, mineral floating, and healthcare. Recently, nanobubbles have been used to explain a mystery puzzled us for over a century, i.e., anesthetics caused by inert gases [4].

However, the phenomenon of stability of nanobubbles is still puzzling although many efforts have been made to understand it. A key aspect for this problem is the structure of gas molecules inside nanobubbles. There is an empirical

equation that shows the relationship between surface tension and densities of a liquid and a vapor, $\gamma = [A(\rho_l - \rho_g)/M]^4$, where M , A , ρ_l , and ρ_g are the molecular weight (kg/mol), parachor, density of liquid (kg/m³), and density of gas (kg/m³), respectively. Based on this relationship, in 2008, Zhang et al. [5] have shown that if density of gas molecules inside nanobubbles is sufficiently large, the life of the nanobubbles in bulk water will considerably increase and even approach the timescale of the experimental observations. At the same time, Wang et al. [6], on the basis of a molecular dynamics simulation, showed that densities of N₂ and H₂ gas bubbles accumulated at water/graphite interfaces greatly increased and reached 41% of the density of liquid N₂ and 52% of that of liquid H₂, respectively, at room temperature and atmospheric pressure. Experimentally, by analyzing the adhesion force data of interfacial nanobubbles using the van der Waals force theory, the gas density near the substrate inside the surface of the nanobubbles was suggested to be about 3 orders of magnitude higher than that under standard pressure and temperature [7]. However, direct evidence from experiments is still lacking.

Very recently, high density inside oxygen nanobubbles on silicon nitride surfaces with lateral size range of 500-800 nm, which is 1-2 orders of magnitude higher than that of gas density in atmospheric pressure, has been reported by Zhou et al. [8]. This result is obtained by analyzing absorption spectra of a single nanobubble using high spatial resolution and chemical identification of synchrotron-based scanning transmission X-ray microscopy (STXM) (Figure 1). Interestingly, the inner density of the nanobubble increases as the

*Corresponding author (email: fanghaiping@sinap.ac.cn)

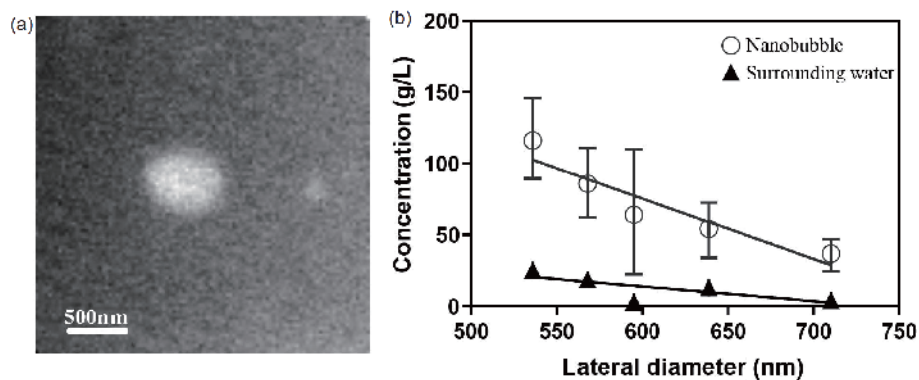


Figure 1 (a) Typical STXM image of a nanobubble; (b) estimated oxygen density inside nanobubbles (cycles) and oxygen concentration in the surrounding water (triangles) near nanobubbles as a function of their lateral diameter (solid lines are a linear fit).

size of the nanobubble decreases and may reach the high density predicted by the molecular dynamics simulations for much smaller nanobubbles. The direct experimental evidence of the high density inside the nanobubble, not only provides a milestone to understand the ultrahigh stability of nanobubbles at the molecular level, but also may demonstrate the existence of a new phase state besides gas, liquid and solid. In addition, this result allows developing novel applications in various fields. For example, with high density, the hypoxia state of a sediment can be effectively improved during the process of water remediation. The survival rate and yield of fries can also be improved in oxygen-rich water, and the high internal concentration may allow efficient gas transportation and gas-related catalytic reactions to occur on a microscale.

Water continues to amaze us. Hydrogen bonding in water is the origin of its anomalous and unique behavior [9,10]. The nanobubble may be another one. To completely understand the stability and physics of nanobubbles in water, studies must be carried out not only regarding the inside

structure of nanobubbles, but also the hydrogen bonding structures at the nanobubble-water interface.

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