Stable bulk nanobubbles can be regarded as gaseous analogues of microemulsions

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Abstract:
In our previous work [Phys. Chem. Chem. Phys. 2022, 24, 9685], we show with molecular dynamics simulations that bulk nanobubbles can be stabilized by forming a compressed amphiphile monolayer at bubble interfaces. This observation closely resembles the stability origin of microemulsions and inspires us to propose here that stable bulk nanobubbles can be regarded as gaseous analogues of microemulsions: the gas-in-water nanobubble phase coexisting with the external gas phase. The stability mechanism for bulk nanobubbles is then given: The formation of compressed amphiphilic monolayer because of microbubble shrinking leads to a vanishing surface tension, and consequently the curvature energy of the monolayer dominates the thermodynamic stability of bulk nanobubbles. With the monolayer model, we further interpret several strange behaviors of bulk nanobubbles: the gas supersaturation is not a prerequisite for nanobubble stability because of the vanishing surface tension, and the typical nanobubble size of 100nm is due to the small bending constant of the monolayer. Finally, through analyzing the compressed amphiphile monolayer model we propose that bulk nanobubbles can ubiquitously exist in aqueous solutions.
**Introduction**

Bulk nanobubbles (BNB) are spherical bubbles of a sub-micrometer size, typically 100 nanometers, suspended in aqueous solution.\(^1\)-\(^4\) Its discovery originated from the early studies on ultrasound and cavitation in 1962.\(^5\) Johnson and Cooke then reported indirect evidence for the existence of bulk tiny bubbles less than 1000 nm in seawater by navy sonar.\(^6\) After 2000, experimental reports on nanobubbles emerged due to the extensive use of advanced experimental techniques, such as dynamic light scattering (DLS), phase microscopy, infrared spectroscopy and nanoparticle tracking analyzers (NTA).\(^7\)-\(^10\) Bulk nanobubbles have aroused strong interest due to their long lifetime and numerous applications, such as water treatment,\(^11\)-\(^14\) agriculture,\(^15\),\(^16\) biomedicine,\(^17\),\(^18\) and micro-reactors.\(^19\)

The unexpected stability of bulk nanobubbles seems to contradict the classical theory. According to the Epstein-Plesset theory,\(^20\) a bubble of 100 nm in radius will have an internal pressure about 14.4 times the atmospheric pressure, and it would dissolve within 1 μs. However, the existence period of observed nanobubbles ranges from several hours to weeks in numerous experiments.\(^4\),\(^7\)-\(^10\) Such a long lifetime indicates that the reported bulk nanobubbles are in fact thermodynamically stable.

Obviously, the classical theory cannot explain the thermodynamic stability of bulk nanobubbles, and new theories are needed. In the past 20 years, the proposed mechanisms for interpreting bulk nanobubble’s stability are mainly divided into two categories: the enrichment of interfacial charges (zeta potential)\(^21\),\(^22\) and the adsorption of contaminants.\(^23\),\(^24\) Although these models are partly capable of
interpreting why bulk nanobubbles are stable, there are some phenomena that cannot be explained by these models: the stability of bulk nanobubbles at low gas saturation or at zeta potential close to 0,\textsuperscript{25-27} and their almost constant size (~ 100 nm) from different reports.\textsuperscript{26-29}

In detail, according to these models the stable radius of nanobubbles always depends on the number of charges and that of contaminants enriched on the nanobubble interface. If the number of charges and contaminants adsorbed can be adjusted in a wide range, stable nanobubbles in any size can be possible. This is inconsistent with experimental observation that the typical nanobubble size is often around 100 nm, regardless of the concentration of the amphiphilic organics or salt solution added.\textsuperscript{26-29} For both the zeta potential mechanism and the contaminant mechanism,\textsuperscript{23} they require the dissolved gas to have a certain level of gas supersaturation, which provides an additional pressure (Laplace pressure) to balance the surface tension of the bubble interface. This is not enough to explain experimental observations that the stable bulk nanobubbles can be observed at rather low gas saturation ($S \sim 0$),\textsuperscript{25} which is common condition in practice due to the exposure of nanobubble solutions to the ambient atmosphere. These disagreements demonstrate the existence of some important characteristics unidentified for the stabilization mechanism of real nanobubbles. Hence, the stabilization mechanism of bulk nanobubbles is still an open question.

In our recent work,\textsuperscript{30} we found that adsorption of amphiphiles (organic contaminants or surfactants) of different structures cause nanobubbles to exhibit
different fates under gas dissolution: stable bulk nanobubble or micelle-like aggregates. With the gas dissolution, the areal density of amphiphiles at the gas-liquid interface of a tiny bubble becomes increasingly high and correspondingly the surface tension decreases. Once the compressed amphiphile monolayer is formed, the bulk nanobubble becomes stable with a vanishing surface tension, even at low gas supersaturation.\textsuperscript{30} The findings demonstrate an obvious similarity between bulk nanobubbles and microemulsions. Microemulsions are known to be thermodynamically stable, with a well-interpreted stability mechanism.\textsuperscript{31-35}

This similarity inspires us to explore the stability theory for bulk nanobubbles, in analogy with microemulsions. By extending our simulation results,\textsuperscript{30} in this work we further propose that bulk nanobubbles can be regarded as gaseous analogues of microemulsions: in microemulsion systems the oil-in-water microemulsion phase coexists with an excess oil phase, while in nanobubble systems it is the gas-in-water nanobubble phase coexisting with the external gas phase (see Figure 1). We then analyze the characteristics of stable bulk nanobubbles from the following aspects: i) The similarity between nanobubbles and microemulsions; ii) The shrinking of large bubbles and the adsorption of amphiphilic molecules lead to the formation of the compressed amphiphilic monolayer at the nanobubble interface; iii) The thermodynamic stability of bulk nanobubbles can be reached once the compressed amphiphilic monolayer is formed; iv) Nanobubble size can be determined from the rigidity of the compressed amphiphile monolayers; v) Trace organic contaminants could be a source of amphiphilic molecules for the formation of compressed
amphiphile monolayer.

I. The similarity between bulk nanobubbles and microemulsions.

![Figure 1](image.png)

Figure 1. The similarity and difference of (a) microemulsions and (b) bulk nanobubbles at small surfactant concentrations. (a) shows the oil-in-water (O/W) microemulsion phase coexisting with an excess oil (O) phase. The whole system is in a two-phase coexistence state (Winsor I type according to Winsor Classification). (b) shows nanobubble-containing aqueous solution that coexists with an excess gas phase. For the oil-in-water microemulsion, the oil droplet (colored in yellow) is encapsulated with a surfactant monolayer in a continuous phase of water, while for the bulk nanobubble, it is the gas bubble is encapsulated with a compressed amphiphile monolayer in the aqueous solution. In both cases, amphiphile molecules (or surfactants composed of a hydrophilic head in red and a hydrophobic tail in black) play an important role in their stability. Our previous simulations indicate that surfactants in the monolayer are in fact in a disordered state.

Microemulsions are thermodynamically stable, isotropic liquid mixtures of two immiscible fluids, typically oil and water, stabilized by amphiphilic surfactants. According to IUPAC definition, a microemulsion is a “dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm”. The typical size of microemulsions is close to the experimentally observed diameter.
(~100nm) of long-lived bulk nanobubbles. As schematically shown in Figure 1a, an oil-in-water (O/W) microemulsion mainly contains three components: solvent (water), surfactant molecules forming the monolayer, and oil molecules that are encapsulated by the monolayer film or are in the excess phase. The whole solution is in a two-phase coexistence state (Winsor I domain in Winsor Classification).\textsuperscript{40} The oil-in-water (O/W) microemulsion phase coexisting with an excess oil (O) phase. Such systems exhibit an ultralow interfacial tension, and so far, the thermodynamic stability and polymorphic coexistence of microemulsions have been well explained.\textsuperscript{34-37}

The similarity between nanobubbles and microemulsions can be summarized as follows: i) They are all nanoscale entities observed in experiments, with a typical size of \textasciitilde100 nm; ii) Both of them are thermodynamically stable. The thermodynamic stabilization of bulk nanobubbles has been recognized through experimental observations,\textsuperscript{26-29} even though the underlying stabilization mechanism is still under debate; iii) Surfactant monolayers on their interfaces play an essential role in their stability. The idea of the existence of surfactant monolayer for bulk nanobubbles is supported by molecular simulations.\textsuperscript{30} Careful experiments\textsuperscript{24} proved that trace organic contaminants are necessary for nanobubble stabilization, and we further demonstrated that a compressed amphiphile monolayer is required for nanobubble stability at low gas supersaturation.\textsuperscript{30} This feature clearly resembles that of microemulsions, for which a surfactant monolayer is required for stability; iv) The vanishing interfacial tension would provide a necessary condition for stability, both for microemulsions and for bulk nanobubbles. For stable bulk nanobubbles at low gas
supersaturation, the vanishing surface tension comes from the dissolution of gas bubbles, which decreases the bubble area and correspondingly decreases the surface tension until an ultralow surface tension is reached.\textsuperscript{30} This is similar to that of microemulsions. Microemulsion is recognized as a thermodynamically stable system, for which the extremely low (nearly zero) interfacial tension is the key for the thermodynamic stability.

Based on aforementioned similarities between bulk nanobubbles and microemulsions, we further propose that stable bulk nanobubbles are a special kind of microemulsion, with simply replacing the oil in the O/W microemulsions with insoluble or slight soluble gas (see Figure 1). Here we will first give the stability mechanism, and then show its ability to interpret some strange behaviors of bulk nanobubbles reported experimentally.

II. The compressed amphiphilic monolayer model and the stabilization mechanism of bulk nanobubbles

The similarity of bulk nanobubbles and microemulsions leads us to propose a compressed amphiphilic monolayer model for bulk nanobubble stability. In this mechanism, we assume that some stable bulk nanobubbles comes from the shrinking of large bubbles, e.g., micro-bubbles.\textsuperscript{41,42} The initial formation of microbubbles can be induced by either swelling of micelles at large gas supersaturation or by macro-bubble collapsing. Then, at low gas supersaturation the gas dissolution causes the shrinkage of the microbubbles until the formation of the compressed amphiphile monolayer at
the bubble interface, which would lead to the formation of stable bulk nanobubbles (see Figure 2).

During the process of microbubble shrinking, the gradual adsorption of amphiphilic molecules and decrease of bubble area would lead to the interfacial enrichment of amphiphiles, for both insoluble or soluble surfactants. For soluble surfactants the enrichment may be because the typical time of surfactant desorption is larger than that for bubble shrinking. The increasing areal density of surfactant at the interface would lead to a decrease in surface tension until a certain value areal density is reached (see Figure 2). Typically, the areal density corresponds to an extremely low (close to 0) surface tension, at which a compressed amphiphile monolayer is formed. When the monolayer is further compressed, decreasing average area occupied by each surfactant would become highly energetic unfavorable. Instead, the monolayer can deform in the normal direction (bending), and therefore, the interfacial free energy per nanobubble is dominated by the curvature free energy.

Figure 2. Schematic drawing of the formation of the compressed amphiphilic monolayer when a microbubble shrinks. The shrinking of a large bubble leads to a decrease in surface tension. Once a minimum in the average area occupied by each surfactant molecule is reached, the compressed
amphiphile monolayer is formed. For the compressed amphiphile monolayer, the interfacial free energy for the nanobubble is dominated by the curvature free energy.

III. The mechanical and chemical equilibriums of bulk nanobubbles with their surroundings

The ultralow interfacial tension can be achieved for the compression amphiphile monolayer,\(^{30}\) which is an important factor for the thermodynamic stability of bulk nanobubbles. With the compressed amphiphile monolayer model, we will show here that both mechanical and chemical equilibrium of dispersed bulk nanobubbles with its environment can be reached, even at a rather low level of gas supersaturation.

Note that we regard the stable bulk nanobubbles as gaseous analogues of microemulsions, namely, the gas-in-water nanobubble phase coexisting with the external gas phase. Therefore, we need to consider a bulk nanobubble dispersed in an aqueous solution that coexists with the ambient gas above the surface of the solution (Figure 1b and also Figure 3). The whole system is in a two-phase coexistence state: the nanobubble-containing solution phase coexists with the ambient gas. The requirement of chemical equilibrium of the gas is schematically shown in Figure 3. The chemical potential of gas in a nanobubble, \(\mu_{g}^{NB}\), can be simplified as ideal gas, and

\[
\mu_{g}^{NB} = \mu_{g}^{sat} + k_{B}T \ln \frac{P_{in}}{P_{sat}}. \\
\mu_{g}^{SOL} \text{ is the chemical potential of gas dissolved in solution,}
\]

and

\[
\mu_{g}^{EN} = \mu_{g}^{sat} + k_{B}T \ln \left( \frac{c_{g}}{c_{g}^{sat}} \right), \text{ } \mu_{g}^{EN} \text{ is the chemical potential of gas in the external gas phase, and}
\]

\[
\mu_{g}^{EN} = \mu_{g}^{sat} + k_{B}T \ln \frac{P_{0}}{P_{sat}}. \text{ In above equations, } P_{0} \text{ is the ambient pressure, } P_{in} \text{ is the pressure of the gas inside the bubble, and } c_{g} \text{ is the actual gas solubility that equilibrates with the bubble. Here a reference state at a pressure of}
\]


\( P_{\text{sat}} \) is chosen with the gas is saturated in solution, and \( \mu_g^{\text{sat}} \) and \( c_g^{\text{sat}} \) are the corresponding chemical potential and the solubility of the dissolved gas.

Therefore, for a nanobubble in the thermodynamic equilibrium state, the equality of chemical potential for gas molecules requires \( \mu_g^{\text{NB}} = \mu_g^{\text{SOL}} = \mu_g^{\text{EN}} \), as shown in Figure 3. This leads to

\[
\mu_g^{\text{NB}} - \mu_g^{\text{SOL}} = k_B T \ln \left( \frac{P_{\text{in}} c_g^{\text{sat}}}{P_{\text{sat}} c_g} \right) = 0, \quad \mu_g^{\text{NB}} - \mu_g^{\text{EN}} = k_B T \ln \frac{P_{\text{in}}}{P_0} = 0.
\]

which give rise to \( P_{\text{in}} = P_0 \) and \( \frac{P_{\text{in}} c_g^{\text{sat}}}{P_{\text{sat}} c_g} = 1 \).

The mechanical equilibrium can be described by the Laplace equation \( \Delta P = \frac{2y}{R} \). The Laplace equation, along with \( P_{\text{in}} = P_0 \) obtained above, gives

\[
\Delta P = \frac{2y}{R} = P_{\text{in}} - P_0 = 0.
\]

This leads to the ultralow surface tension \( (\gamma \approx 0) \). Therefore, the vanishing surface tension is a consequence of the thermodynamic (both mechanical and chemical) requirement for stable bulk nanobubbles.

Then we analyze what \( \frac{P_{\text{in}} c_g^{\text{sat}}}{P_{\text{sat}} c_g} = 1 \) means. We define \( S \) as the supersaturation of the gas at ambient pressure \( P_0 \), and \( S = c_g / c_g^0 - 1 \), with \( c_g^0 \) the saturated solubility at ambient pressure \( P_0 \). According to Henry’s law, \( c_g = HP_{\text{in}} \) and \( c_g^0 = HP_0 \), with \( H \) the coefficient of Henry’s law. Thus, we have \( SP_0 = P_{\text{in}} - P_0 \approx 0 \), which means \( S \approx 0 \). This is consistent with the experimental observations that even at low gas supersaturation \( (S \approx 0) \), a large number of bulk nanobubbles can exist stably.\(^{25}\)
IV. Nanobubble size can be estimated from the rigidity of the compressed amphiphile monolayers.

Then we turn to the question of why the typical size of nanobubble observed experimentally is almost around 100nm, and illustrate how this observation can be explained from the compressed amphiphile monolayer model?

First, we stress again that once the compressed amphiphile monolayer is formed, the monolayer is tensionless but shows the tendency to resist certain changes in its curvature. This is because for the compressed monolayer, although a general deformation of monolayer involves both a change of area and curvature, the further change of monolayer area would become energetic unfavorable. Since the compressed monolayer can also deform more easily in the bending modes, the
interfacial free energy of the nanobubble is dominated by the curvature free energy. This curvature energy for tensionless monolayer having a curvature that deviates from its spontaneous curvature was emphasized by Helfrich. Here we apply Helfrich model to interpret the thermodynamic stability of bulk nanobubbles, with which the interfacial free energy of the surfactant monolayer reads,

\[ F_0 = \int \left[ f_0 + \frac{\kappa}{2} (c_1 + c_2 - 2c_0)^2 + \bar{\kappa} c_1 c_2 \right] dA. \]  

(3)

Here \( f_0 \) can be related to the surface tension of the planar interface by \( \gamma_0 = f_0 + \frac{\kappa}{2} c_0^2 \). The spontaneous curvature, \( c_0 = 1/R_0 \) with \( R_0 \) the spontaneous radius of curvature, reflects the asymmetry between the inside and outside of the monolayer. The above expression for the bending energy serves as definition of two material constants of the monolayer, the bending moduli, \( \kappa \) and \( \bar{\kappa} \), which are also called bending rigidity and saddle-splay modulus, respectively. For a spherical nanobubble, \( c_1 = c_2 = 1/R \), and we have

\[ F_0 = \int \left[ \gamma_0 - 4\kappa \left( \frac{1}{R} \right)^2 + (2\kappa + \bar{\kappa}) \left( \frac{1}{R} \right)^2 \right] dA. \]

In general, the spontaneous curvature \( c_0 \) and the bending stiffness \( \kappa \) of surfactant monolayers are two important factors that determine the stability size of spherical nanobubble, just as for the stability of microemulsions. \( \kappa \) is strongly decreased when mixtures of surfactants of different chain lengths are used, because of the resulting disorder of surfactant chains. Szleifer et al. found that for one-component surfactant membrane the curvature elastic constant can vary from \( k_B T \) to tens of \( k_B T \) by increasing chain length or by decreasing the area per molecule. More significantly they found that addition of relatively short-chain alcohol and other co-surfactant additives is sufficient to lower the bending constant by an order of
magnitude. Based on these findings, we believe that there exist two different situations for the compressed amphiphilic monolayers, depending on the experimental conditions (see Figure 4).

Figure 4. The schematic drawing of two different models for the compressed amphiphile monolayer: (a) The monolayer composed of only long-chain-surfactant molecules, and (b) the monolayer contains both long-chain and short-chain surfactant molecules.

For the first case (Figure 4a), it is the large and insoluble surfactants of same type that compose of the monolayer. In this case, the stiffness $\kappa$ of the compressed monolayer for bulk nanobubbles is rather large ($\kappa \gg 1/k_B T$). With eq 3, the minimization of $F_s$ with respective to bubble radius at constant total area $A$ (or equivalently, the fixed number of surfactant molecules at the nanobubble interface) leads to a relation between the optimal bubble radius $R_e$ and the spontaneous radius of curvature $R_0$:

$$\frac{R_e}{R_0} = \frac{2\kappa + \bar{\kappa}}{2\kappa}. \quad (4)$$

Therefore, when the stiffness $\kappa$ of the monolayer film is large ($\kappa > 10/k_B T$), the minimized bending free energy $F_s$ will drive the equilibrium size of the nanobubble approaching $R_0$ since $\bar{\kappa}$ is a relatively small in magnitude. In other words, for stiff monolayers it is the spontaneous curvature $c_0 = 1/R_0$ that determines the size...
of bulk nanobubbles. \( c_0 \) or \( R_0 \) can be directly related to the shape of amphiphilic molecules, indicating the tendency of the interface to curve toward either the water \((c_0 > 0)\) or the gas \((c_0 < 0)\). As shown in our molecular dynamic simulations,\(^{30} \) \( c_0 < 0 \) is required for stable nanobubbles.

The second situation is for the multi-component amphiphile monolayer (Fig. 4b), in which the mixing of long-chain-surfactant and short-chain-surfactant (e.g., alcohol) lowers substantially the bending constant \( \kappa \).\(^{44} \) We believe that the trace organic contaminant-stabilized bulk nanobubbles belongs to this situation. When \( \kappa \) is small enough (~\( k_B T \)), the thermal motion becomes one of dominating factor determining bubble size. The competition between thermal and bending energy can be described by the notion of persistence length \( \xi_k \), which plays an essential role in determining the nanobubble size, as for the microemulsions.\(^{34-36} \) For isotropic film of microemulsions, de Gennes and Taupin proposed that the droplet size will be determined by the persistence length \( \xi_k \) of the interface:\(^{34} \) at scales smaller than \( \xi_k \) the interface is essentially close to flat, whereas at scales larger than \( \xi_k \) it is strongly wrinkled. Similarly, for spherical nanobubble we can assume that \( \xi_k \) is related to the rigidity \( \kappa \) by \(^{35,36,47,48} \)

\[
\xi_k = \xi_0 \exp\left(\frac{4\pi}{3k_B T}\right)
\]

where \( \xi_0 \) is a molecular length close to the surfactant layer thickness.

Here, we determine the persistence length \( \xi_k \) for bulk nanobubbles by setting the typical stiffness of flexible surfactant monolayers around \( 1k_B T \),\(^{34-36,43-44} \) i.e., \( \kappa \sim k_B T \). When we choose the typical value for surfactant monolayer \( \xi_0 = 10\text{Å} \) and \( \kappa = \)
eq 5 gives $\xi_k \approx 65.8 \text{nm}$. For a bulk nanobubble, it is spherical and $R \sim \xi_k$. Thus, the bubble size predicted from the compressed amphiphilic monolayer model is roughly consistent with the experimentally observed values that are mostly around 100 nm (diameter).

If the stiffness $\kappa$ of the monolayer is further reduced, $\kappa$ is smaller than $k_B T$. $\xi_k$ is of the order of a molecule length. In this case, the shape and thermal fluctuation of the monolayer dominates, well-defined surfactant monolayers are unable to form. Thus, the nanobubble structure becomes unstable, and one would obtain a micelle-like structure.$^{30}$

Above, we distinguish two different situations, both leading to compressed amphiphile monolayers that can stabilize bulk nanobubbles. However, they applied to different situations. For the first one, the one-component rigid monolayer model, it may apply to systems with insoluble surfactants of a single type (e.g., lipid). In this case, the bulk size is mainly controlled by the spontaneous radius of curvature, $R_0$, which is directly related to the shape of an amphiphilic molecule (the packing parameter of amphiphilic molecules). For trace organic contaminant-stabilized bulk nanobubble systems, for which most bulk nanobubbles are experimentally reported, we prefer the second situation, i.e., the multi-component soft monolayer. In this model, the multi-component monolayer is featured with a lower bending constant. Under the condition of $\kappa \sim k_B T$, at which thermal and bending energy are of comparable contributions, the persistence length $\xi_k$ or bubble size would have a size around 100nm. In case of $\kappa \ll 1 k_B T$ the nanobubbles would become unstable and micelle-like structures are
V. The ubiquitous existence of bulk nanobubbles in aqueous solutions

Above analysis shows that the existence of compressed amphiphile monolayer is essential for the long-lived nanobubbles. Then an open question raises: for the compressed amphiphile monolayer, where do the amphiphilic molecules come from? Here, we illustrate that even trace organic contaminants in solution can be one of source of amphiphilic molecules to stabilize bulk nanobubbles. Then we propose that the bulk nanobubbles can ubiquitously exist in aqueous solutions.

A carefully experimental work\textsuperscript{24} shows that concentration of the generated bulk nanobubbles becomes negligible if pure water was used, the equipment was cleaned properly, and certain plastic materials were avoided. The results indicate that trace organic contaminants are necessary for nanobubble stabilization. At present there is no technique available that is able to identify where the amphiphilic molecules (contaminants) come from: from gas source, from the solution surface exposure to airborne contaminants or from the solution itself.

Here we just illustrate that even under typically experimental conditions, the small amount of the trace organic contaminants dissolved in the so-called “pure” solvent is sufficient to supply the amphiphile molecules for stabilizing a large number of bulk nanobubbles. Many experiments reported the observation of stable nanobubbles in the typically pure water (<50ppb) system, and the concentration of bulk nanobubbles is mostly around $c_{NB} \approx 10^9/mL$,\textsuperscript{26-29} with a typical bubble size around 100nm.
For analyzing whether this small level of contaminants is sufficient to stabilize the bulk nanobubbles, we take the radius of the nanobubble as 50nm and assume that the cross-sectional area $a$ of the surfactant molecule is about 9 Å$^2$. For a single nanobubble of 100 nm, the number of surfactants $n_1$ required for the compressed monolayer can be estimated as $n_1 = \frac{4\pi R^2}{a} \approx 3.49 \times 10^5$. The total number of surfactants needed for all bulk nanobubbles in 1mL solution is about $N_1 = n_1 c_{NB} \approx 3.49 \times 10^{13}$.

Then we estimated the amount of surfactant existed in the solution from the reported carbon content (TC). In nanobubble experiments the TC of pure water is often given, with a typical value of <50 ppb. Here we chose a typical value of 24 ppb. Since the carbon content mainly comes from organic contaminants in the solution, which is assume to act as surfactants. Thus, we can approximate the concentration of surfactants (contaminants) in water, $c_{surf}$, by the given TC. The total number $N_2$ of surfactants actually contained in 1mL of water can be estimated by $N_2 = \frac{1g \times c_{surf}}{M_{surf}} N_A \approx 5 \times 10^{13}$. Here $M_{surf}$ is the molar mass of the surfactant, having a value of 288 g/mol with reference to SDS, and the Avogadro’s constant $N_A = 6.02 \times 10^{23} mol^{-1}$.

We assume that 60% of the TC is regarded as consisting of surfactant, $N'_2 = N_2 \times 60\% \approx 3 \times 10^{13}$. It is clear that $N'_2 \approx N_1$, meaning that even for the ultrapure water used in experiments, it still contains the sufficient amount of contaminants that is able to stabilize the bulk nanobubbles with a typical concentration of $c_{NB} \approx 10^9/mL$ reported experimentally.

Note that this is just a rough estimate, without considering the distribution of the organic contaminants between dissolution and interface adsorption (one side is the
atmosphere). If the distribution is taken into account, the concentration of stable bulk nanobubbles would decrease. This is also consistent with the experimental observations that the concentration of bulk nanobubbles can be substantially reduced if the solution is carefully prepared to remove the organic contaminants.\textsuperscript{24} However, the trace organic contaminants in solution itself are not the single source of amphiphilic molecules. Organic contamination may also come from other sources. For example, the solution surface and the container exposure to airborne contaminants, both may introduce contaminants. Several reports showed that graphite surfaces exposed to air may accumulate a thin organic layer.\textsuperscript{50-53}

With the compressed amphiphile monolayer, we can predict the ubiquitous existence of bulk nanobubbles in aqueous solution, with a more or less bubble concentration. This ubiquity is based on the following facts: unavoidable existence of trace organic contaminants that act as a source of amphiphiles, and the interface adsorption of amphiphiles and shrinking of large bubbles that leads to the formation of compressed amphiphile monolayer, and the bulk nanobubbles with such a monolayer are thermodynamically stable. Therefore, we can safely conclude that the appearance of bulk nanobubbles can be much more commonly found than we expected.

Note that although the compressed amphiphile monolayer mechanism can explain many experimental observations of nanobubble stability, it does not mean that this model can be applied to all cases of bulk nanobubbles. In particular, for bulk nanobubbles with high interfacial charge density, the zeta potential would play an
important role in their stability. For nanobubbles in a solution with high gas supersaturation, similarly the vanishing surface tension and thus the compressed amphiphile monolayer are not needed for their stability.

Conclusions

Numerous experiments show that the lifetime of observed bulk nanobubbles ranges from hours to weeks, indicating that these nanobubbles are in fact thermodynamically stable. However, the stabilization mechanism of bulk nanobubbles is still an open question, and at least some experimental observations cannot be explained: the stability of bulk nanobubbles at low gas saturation, as well as the stable nanobubbles reported experimentally having a typical size around ~100 nm. Our previous work demonstrated through molecular dynamics simulations that bulk nanobubbles can be stabilized by forming a compressed amphiphile monolayer at bubble interfaces. This observation closely resembles stability of microemulsions. This similarity inspires us to explore the stability theory for bulk nanobubbles, in analogy with microemulsions.

In this work we further proposed that nanobubbles can be regarded as gaseous analogues of microemulsions (or more directly as a special kind of microemulsions), through replacing oil in microemulsions with gas. Thus, the whole nanobubble-containing solution is in a two-phase coexistence state: the gas-in-water nanobubble phase coexisting with the external gas phase. The stability mechanism for bulk nanobubble can be summarized as follows: The shrinking of large bubbles and the
adsorption of amphiphilic molecules lead to the formation of a compressed amphiphilic monolayer at the interface of bulk nanobubbles. The compressed monolayer is featured with an ultra-low surface tension, and thus it is the curvature free energy, rather than surface tension, that dominates the interface free energy.

With the compressed amphiphile monolayer model, we then analyze the thermodynamic (both mechanical and chemical) equilibrium of bulk nanobubbles with their surroundings. The unexpected stability of bulk nanobubbles at rather low gas saturation can be well interpreted as a result of the formation of the compressed amphiphilic monolayer, which is in fact tensionless. Therefore, gas supersaturation is no longer a necessary condition for stability of bulk nanobubbles.

Then, we explain why the typical size of stable bulk nanobubbles reported is often around 100nm. We propose that for most experimentally reported bulk nanobubbles that are stabilized by the adsorption of trace organic contaminants, the multi-component nature of the monolayer leads to a very low bending constant $\kappa$ due to the effect of chain disorder. At such a small $\kappa$, the thermal fluctuation is of a comparable contribution as the bending energy. Under conditions of $\kappa \sim k_B T$, a simple estimate from persistence length predicts a size of stable nanobubble sizes that are around 100 nm (diameter). If $\kappa \ll 1k_B T$ the bulk nanobubbles would become unstable and we expect the disappearance of the nanobubbles within a short time.

Finally, we demonstrate that bulk nanobubbles can ubiquitously exist, even in so-called “pure” water. We illustrate that even the small amount of the trace organic contaminants dissolved in the chemically “pure” solvent is sufficient to supply the
amphiphile molecules needed for stabilizing bulk nanobubbles at a typical nanobubble concentration $c_{NB} \sim 10^9/\text{mL}$. In real situation, there exist more sources of organic contaminants that can introduce amphiphilic molecules into the solution, which tend to stabilize bulk nanobubbles.

Thus, the ubiquitous existence of bulk nanobubbles is a direct consequence of the compressed amphiphile monolayer model: unavoidable existence of trace organic contaminants that act as a source of amphiphiles, and the interface adsorption of amphiphiles and shrinking of large bubbles that lead to the formation of compressed amphiphile monolayer, and the bulk nanobubbles with such a monolayer are thermodynamically stable. The ubiquitous existence of bulk nanobubbles in aqueous solutions may have significant effects on a variety of processes that are related to bubble formation and disappearance.

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