Technical Physics Letters, 2022, Vol. 48, No. 5

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The effect of electrostatic pressure on the diffusion equilibrium of bulk nanobubbles

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Received February 14, 2022
Revised March 9, 2022
Accepted March 9, 2022

A modified formula for calculating the electrostatic pressure (EP) in bulk nanobubbles (BNB) is proposed. It is shown that EP prevents the diffusion dissolution of BNB in an aqueous solution. As a result, the BNB dissolves only partially and becomes stable.

Keywords: nanobubbles, Henry's law, double electric layer, lifetime

DOI: 10.21883/TPL.2022.05.53468.19166

A number of experimental and theoretical studies of bulk nanobubbles (BNB) has increased sharply in recent years [1–11] due to their wide application in various fields of science and technology. It is believed that the main stabilizing factor of BNB are the ions adsorbed on its surface. Electrokinetic potential, on the one hand, prevents BNB coagulation, and, on the other hand, creates a tensile negative electrostatic pressure (EP) that compensates for the compressive Laplace pressure (LP) and prevents diffusive dissolution of the BNB [1–3,7–9].

However, this viewpoint is not universally accepted. In [4] it is argued that EP cannot stabilize BNB due to its smallness compared to LP. Alternative theories, which, in our opinion, do not stand up to criticism (see [2]), have been proposed in papers [10,11]. The theory developed in [2] is valid for the special case when ionic strength of the solution is negligible (see discussion below). According to experiments [6], when the electrokinetic potential of the double electric layer (DEL) is zero, BNBs collapse with the formation of free radicals. In accordance with this, as well as many other experiments, the EP is the main, if not the only, stabilizing factor for the BNB.

The purpose of the present paper is to show theoretically that EP causes diffusive stabilization of BNB.

When a BNB is formed in a liquid medium (distilled water, dilute aqueous electrolyte solution, a mixture of water and ethanol, etc.), a DEL is formed around it. Electrostatic energy W of such layer may be described with a formula of a spherical capacitor

$$W = \frac{q^2}{2C} \tag{1}$$

with electric capacity C, equal to

$$C = 4\pi\varepsilon_0\varepsilon\frac{R(R + L_D)}{L_D}, \tag{2}$$

where

$$L_D = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{2IN_A e^2}} \tag{3}$$

— Debye shielding length, q — charge on a nanobubble surface, R — its radius, e — elementary charge, k_B and N_A — — Boltzmann's constant and Avogadro number, respectively, T — absolute temperature, ε — dielectric permeability of water, ε_0 — electric constant,

$$I = \frac{1}{2}\sum_i c_i z_i^2 \tag{4}$$

— solution ion strength, c_i and z_i — mole concentration and charge (in units e) of ith ion.

In case of meeting the condition

$$L_D \gg R \tag{5}$$

for electrostatic energy, equation is produced from (1), (2)

$$W = \frac{q^2}{8\pi\varepsilon_0\varepsilon R}. \tag{6}$$

If we suggest that in process of radius variation the charge remains stable, for EP p_e, which performs the work to expand BNB, equal to the change with reverse sign of electrostatic energy $(-dW)$,

$$p_e 4\pi R^2 dR = -dW, \tag{7}$$

from (6), (7) the known equation is produced [1–4,7,8]:

$$p_e = \frac{q^2}{32\pi^2\varepsilon_0\varepsilon R^4} = \frac{\sigma^2}{2\varepsilon_0\varepsilon}, \tag{8}$$

where

$$\sigma = \frac{q}{4\pi R^2} \tag{9}$$

— surface density of the charge. Therefore, the common equation for EP (8) is only fair, when inequality (5) is complied with, i.e. practically with complete absence of ions ($c < 10^{-6}$ M, see table). Accordingly, in this case the BNB stability theory is applicable, which is developed in [2].

In another limit case

$$L_D \ll R \tag{10}$$

from (1), (2) we have

$$W = \frac{q^2 L_D}{8\pi\varepsilon_0\varepsilon R^2}. \tag{11}$$

For EP from (7) it is

$$p_e = \frac{q^2 L_D}{16\pi^2\varepsilon_0\varepsilon R^5} = \frac{\sigma^2 L_D}{\varepsilon_0\varepsilon R}. \tag{12}$$

For a random value of Debye length L_D from (1), (2), and (7) we have

$$p_e = \frac{(2R + L_D)q^2 L_D}{32\pi^2\varepsilon_0\varepsilon R^4 (R + L_D)^2}. \tag{13}$$

From (13) the ratios (8) and (12) follow as private cases.

Let us consider occurrence of BNB. Let the solution initially have an excess concentration (mole fraction) $x_{\max}$ of some dissolved gas (nitrogen, air, oxygen, etc.), and after removal of supersaturation the concentration dropped to the value $x_{\min}$. In this case, so-called critical BNBs with gas pressure $p_{\max} = k_H x_{\max}$ (k_H — Henry's factor of the dissolved gas) are formed in the solution. According to the vast majority of experiments [3–8], the ionic force is such that inequality (10) is most often satisfied. The mechanical equilibrium condition for the so-called critical BNB nuclei formed is

$$\frac{\sigma^2 L_D}{\varepsilon_0\varepsilon R_{cr}} + p_{\max} = \frac{2\gamma}{R_{cr}} + p_a. \tag{14}$$

Here p_a — pressure in the liquid (often equal to normal atmospheric pressure), γ — surface tension at the solution−gas boundary (dependence of γ on radius R will be neglected for simplicity). The critical nucleus size is

$$R_{cr} = \frac{2\left(\gamma - \frac{\sigma^2 L_D}{2\varepsilon_0\varepsilon}\right)}{p_{\max} - p_a} \approx \frac{2\gamma}{p_{\max} - p_a}. \tag{15}$$

The second approximated equality is met because of EP smallness compared to LP for a critical nucleus. After removal of supersaturation, BNB starts dissolving in water, however, its dissolution will be prevented by rising EP p_e. Let us introduce a few assumptions.

1. In process of gas diffusion from BNB, its surface charge

$$q_{cr} = 4\pi R_{cr}^2 \sigma \tag{16}$$

remains constant with a varying radius. Then, if in equation (12) the charge q is substituted with q_{cr} from (16), for EP p_e you can write

$$p_e(R) = \frac{\sigma^2 R_{cr}^4 L_D}{\varepsilon_0\varepsilon R^5}. \tag{17}$$

2. In process of BNB dissolution the mechanical equilibrium remains.

With the assumptions made, the equation for gas pressure in process of BNB dissolution will be rewritten as

$$p = \frac{2\gamma}{R} + p_a - \frac{\sigma^2 R_{cr}^4 L_D}{\varepsilon_0\varepsilon R^5}. \tag{18}$$

Diffusion equilibrium will establish when gas pressure in BNB becomes equal to the value $p_{eq} = k_H x_{\min}$ (equilibrium BNB). The calculation performed under (18), demonstrates (Fig. 1) that pressure reaches maximum at radius $R_{\max}$, meeting the ratio

$$\frac{R_{\max}}{R_{cr}} = \sqrt[4]{\frac{5\sigma^2 L_D}{2\varepsilon_0\varepsilon\gamma}} < 1. \tag{19}$$

Since $R_{cr} > R_{\max}$, for a critical nucleus LP dominates above EP (see (15)). From Fig. 1 you can also see that after formation of a critical BNB the pressure rises from $p_{\max} = 4 \cdot 10^5$ to $1.1 \cdot 10^6$ Pa, and then drops to equilibrium $p_{eq} = 0.8 \cdot 10^5$ Pa.

If we assume that gas inside BNB is ideal, from (18) we will get the equation for the number of molecules N inside BNB

$$N = \frac{4\pi}{3k_B T}\left(2\gamma R^2 + p_a R^3 - \frac{\sigma^2 R_{cr}^4 L_D}{\varepsilon_0\varepsilon R^2}\right). \tag{20}$$

Results of the calculation presented in Fig. 2 demonstrate that after formation of a critical BNB the radius R monotonously reduces because of diffusion (reduction of N), until it reaches equilibrium value R_{eq}. Since equilibrium pressure depends on Henry's constant k_H and gas concentration value after removal of supersaturation $x_{\min}$, the size of equilibrium BNB R_{eq} should depend on gas type.

Time of BNB dissolution may be estimated using formula [1,12]:

$$\tau_b = \frac{k_H R^2 M}{3N_A k_B T D\rho}. \tag{21}$$

Here ρ — solution density, M — its „molar“ weight (for dilute solutions that we consider this is just density and molar weight of water), D — coefficient of gas molecule diffusion in water. When boundaries water−BNB change,

Calculation of Debye length L_D using formulas (3), (4) for a binary solution at different concentrations of ions ($z_1 = z_2 = 1$, $c_1 = c_2 = c$, $T = 298$ K)

c, M	L_D, nm
10^{-6}	308
10^{-5}	97.4
10^{-4}	30.8
10^{-3}	9.7
10^{-2}	3.1
10^{-1}	0.97
1	0.31
10	0.1

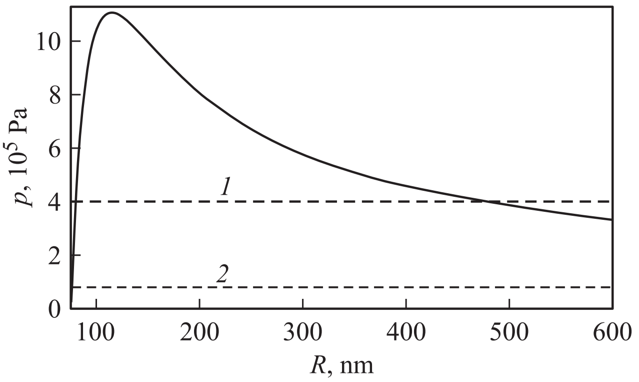

Figure 1. Dependence of pressure in BNB p on radius R after removal of supersaturation. Calculation under formula (18). Parameters: $z_1 = z_2 = 1$, $c_1 = c_2 = c = 0.1\,\mathrm{M}$, $\varepsilon = 81$, $T = 298\,\mathrm{K}$, $\gamma = 0.072\,\mathrm{J/m^2}$, $\sigma = 0.0083\,\mathrm{C/m^2}$, $p_a = 10^5\,\mathrm{Pa}$. Dotted line *1* — gas pressure inside a critical nucleus $p_{\max} = k_H x_{\max} = 4 \cdot 10^5\,\mathrm{Pa}$ (corresponding radius $R_{cr} = 480\,\mathrm{nm}$), dotted line *2* — gas pressure inside equilibrium BNB $p_{eq} = k_H x_{\min} = 0.8 \cdot 10^5\,\mathrm{Pa}$ (corresponding radius $R_{eq} = 76\,\mathrm{nm}$). Curve $p(R)$ reaches maximum at $R_{\max} = 115\,\mathrm{nm}$. The calculation was done for nitrogen ($k_H = 9.2 \cdot 10^9\,\mathrm{Pa}$).

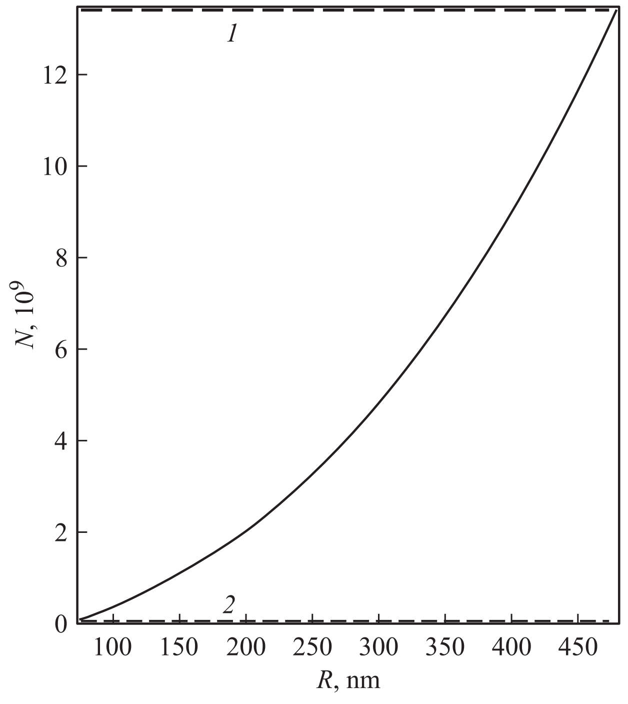

Figure 2. Dependence of molecule number in BNB N on radius R after removal of supersaturation. Calculation under formula (20). All parameters are the same as in Fig. 1. Dotted line *1* corresponds to the number of molecules $N_{cr} = 1.34 \cdot 10^{10}$ in a critical nucleus of BNB with radius $R_{cr} = 480\,\mathrm{nm}$, dotted line *2* — to the number of molecules $N_{eq} = 3.6 \cdot 10^4$ in an equilibrium nucleus of BNB with radius $R_{eq} = 76\,\mathrm{nm}$.

DEL readjusts. Time τ_d, necessary for this process may be estimated approximately, having divided the Debye length L_D by certain averaged thermal speed of ions $\upsilon_{th} = \sqrt{\frac{3k_B N_A T}{M_i}}$:

$$\tau_d = \frac{L_D}{\upsilon_{th}}. \tag{22}$$

To estimate the upper border of value τ_d you can assume that M_i is molar weight of the heaviest ion forming DEL. Calculation under formulas (21), (22) with condition (10) demonstrates that the inequality is met with high margin

$$\tau_b \gg \tau_d.$$

From calculations under formulas (21), (22) it follows that value τ_b — specific time of BNB size variation — by 6–8 orders of magnitude exceeds τ_d. It means that whenever BNB size changes, DEL manages to readjust instantly.

Therefore, when Debye length smallness condition is met (10), the equation for EP is (12). The critical BNB emerging after removal of supersaturation starts dissolving, however, due to rising EP, which compensates LP, the dissolution will be suspended, and BNB will become equilibrium.

Conflict of interest

The author declares that he has no conflict of interest.

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