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Research Article

Do Nanobubbles Survive after Boiling?

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Abstract

The effect of diluting and boiling water solutions with nanobubbles (NBs) was examined. Dilution results in lower concentrations of NBs and boiling results in higher concentrations than expected. In both cases, the size of the bubbles is scattered, but not drastically, whereas the concentration decreases with dilution. Optical and spectra measurements were conducted in this study. The mechanism of NB survival is outlined. Bulk NBs are displaced by water bubbles that are much larger, but of the same charge, into their wake and prevent them from reaching the surface and bursting. During boiling, surface NBs are detached from the vessel walls and collide with the bulk of the solution. In this way, the concentration of bulk NBs increases and the size of the NBs changes randomly.

Keywords: nanobubbles; boiling point; stability; dilution

1. Introduction

Nanobubbles (NBs) are tiny gaseous cavities that are commonly less than 0.5 μm in size [1]. According to the diffusion theory [2], they should not exist for more than a few milliseconds, yet they do exist and, moreover, they can last for weeks, even months [3]. To demonstrate this contradiction, we present all three possible situations [4]. First, we assume an undersaturated solution where the gas concentration far away from the bubble is less than that at the bubble–liquid interface. In this case, the NBs will shrink and dissolve. Next, we assume an oversaturated solution where the concentration far away from the bubble is greater than that at the interface. In this case, the NBs will grow and burst. Finally, we consider an even solution where both concentrations are equal. In this case, the system is unstable, and the slightest disturbance will cause the bubble to either expand or dissolve. Experience defies these predictions [5].

Currently, NBs are classified into bulk (bNBs) and surface (sNBs). The main difference is the lack of a three-phase contact line for the former compared to the latter [6]. Therefore, bNBs are mobile while sNBs are not. Additionally, the radius of curvature of bNBs is much smaller than that of sNBs. The thermodynamic stability of NBs has been the subject of intense debate [7-21]. There is now a consensus on the existence of sNBs [22-24], but for bNBs, the situation remains under dispute [25-28].

Although there are scientific reservations regarding the existence of bNBs, the market is already celebrating the use of them in many industrial processes such as water treatment, the food industry, biochemistry, drug delivery, agriculture, and hydropony [29-33]. According to the Fine Bubble Industries Association and the Wall Street Journal, the market for NBs has increased from $20 million in 2010 to $20 billion in 2020 [34]. In Europe, business is expected to grow from €72 million in 2020 to €145 million by 2030 [35].

In this study, we examined the fate of NBs after boiling. Intuitively, it was expected that boiling would diminish the concentration of NBs, because the rising water bubbles would drag them to the surface and burst. However, the reality was different.

2. Experimental Section

Oxygen NBs in deionized water (DI) were produced by using a home-made generator. Initially, water was mixed with pressurized oxygen to generate bubbles in the liquid. The said bubbles produced at this stage progressively decayed in the first generator to microbubbles (MBs). Then, by passing the liquid through a second generator with a porous plug head, NBs were produced. Full details on this method are described elsewhere [36].

Apparently, the obtained solution contained the maximum possible concentration of NBs that this particular method could produce. We denoted this solution as 100% and used it as the basis for the production of three more diluted solutions with nominal concentrations of 75%, 50%, and 25%. The concentration of NBs was then measured with the aid of Malvern Nanosight LM10 [37]. After that, 100 mL of each of the aforementioned solutions was boiled using ASTM equipment [38] for about 30 min until almost half of the solution had evaporated, and the remaining portion of the solution was measured in the same way as the non-boiled ones. To reconfirm the effect of boiling, UV absorption of the solutions, before and after boiling, was conducted. For this purpose, a Shimadzu UV-1900 spectrometer was employed [39]. Measurements on DI water (i.e., without NB) were conducted for reference purposes, and then the light scattering spectra of the samples were collected.

The masses of the solutions before and after boiling were determined up to the fourth decimal point, and the exact concentrations inter-related with the nominal ones were calculated (Table 1). It is important to note that the results before and after boiling changed from sample to sample and time to

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time. To compensate for this, the following supplementary measurements were conducted: (i) DI water was examined before and after boiling for possible micro/nano-bubbles; (ii) DI water with NBs before boiling was examined on the 1st, 3rd, 5th, and 7th days to determine the changes in the concentration and size of NBs; (iii) the previous samples were boiled and examined for NBs on the same given day; and (iv) the 100% boiled solution was re-examined on the 5th day after 12 days without boiling. In all cases presented in this study, the samples were left to cool down to ambient temperature after boiling before measurements were conducted. Having a reference temperature and pressure is though to be important because the stability of the NBs as well as their thermodynamic properties probably depend on these parameters.

3. Results and Discussion

Figure 1 shows the experimental results (blue/red points) against the expected results (blue/red broken lines). Expected curves were calculated as follows: a) In the case of dilution (blue broken), the 100% (or 100 mL) nominal solution had an initial concentration of NBs that was measured to be equal to $182x10^6$NB/mL (see Table 1); hence, for the 25% dilution (or 25 mL of the nominal solution plus 75 mL of DI water), the value was $0.25x182x10^6$NB/mL=$45x10^6$NB/mL. b) In the case of condensation (red broken), 100 mL of the 25% dilution was boiled until 57% had evaporated. The expected NB concentration of the remaining 43% was calculated based on the measured concentration for the 25% solution before boiling; hence, $35x10^6$NB/mL/0.43=$81x10^6$NB/mL. Calculations were applied on the exact percentage values of the solutions, not on the nominal ones, although the values were similar.

Figure 1 (blue points) illustrates the dilution of the initial NB solution (denoted 100%) to the other three concentrations (denoted 75%, 50%, and 25%). Apart from the 100% case which, as the relative basis of the derivative solutions, could not be differentiated, the NB populations in the other solutions followed an exponential decay (black line).

The population was smaller than expected (blue broken line), but this deviation does not violate the expected trend. The concentration of NB decreased with dilution. The results indicate that, during transfusion from one vessel to the other, some of the NBs do not intervene; either they break or turn from bulk to surface NBs and stack on the vessel walls. For instance, having many bNBs present in a solution helps with their stabilization as they form clusters [40]. Since dilution is an exothermic process, some clusters may dissociate, favouring a bNB→sNB direction as a surviving possibility, causing the dilution to decline more than the expected values.

Figure 1 (red points) illustrates the effect of boiling. The concentration of NBs follows an exponential decay (black line). The population was larger in all four solutions compared with that expected (red broken) but without violating the expected trend. In all cases, the concentration of NBs decreased with dilution. This result indicates that, after boiling, NBs not only survive but may also increase in number. However, the standard errors for the cases after boiling were greater than that before boiling, one reason for this being the non-uniform nature of the boiling process. Table 1 summarizes these findings.

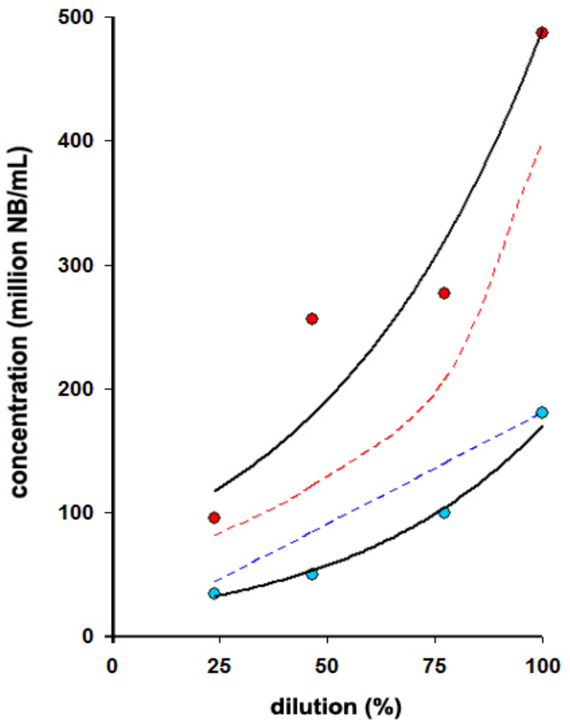

Fig 1. Concentration of NBs vs. dilution %. Blue points: before boiling, blue broken line: expected values, solid black line: exponential fit of the experimental data. Red points: after boiling, red broken line: expected values, solid black line: exponential fit of the experimental data (see also text for details).

Table 1. NB solutions.

Nominal Solution (%)	Measured Solution (%)	Concentration Before boiling (10^6 NB/mL)	Concentration After boiling (10^6 NB/mL)	Size of NBs Before boiling (nm)	Size of NBs After boiling (nm)
25	24	35 ± 8	95 ± 15	267 ± 34	334 ± 9
50	47	49 ± 8	256 ± 56	195 ± 22	319 ± 28
75	77	99 ± 28	277 ± 25	229 ± 29	196 ± 29
100	100	182 ± 19	487 ± 90	215 ± 19	161 ± 40

We confirmed these results by measuring the UV absorption of all solutions before and after boiling (Figure 2). After boiling, the scattering of the samples was stronger than that before boiling, indicating an increase in the concentration of NBs. This is in accordance with the results presented in Figure 1 and Table 1, that is, the concentration of NB increases after boiling. Before boiling, the UV spectra showed a peak at about 220 nm; this peak disappeared for the 25% solution. After boiling, the peak was more like a hump at about the same wavelength and it faded as dilution progressed. This result indicates that the size of the NBs ranged more broadly in the case after boiling than in the case before boiling.

Because the results collected before and after boiling changed over time, we constructed 3D plots for both size and concentration at different time periods (Figure 3) to identify any prevailing trends. To make the plots comprehensive, it is important to clarify that 1st, 3rd, 5th, and 7th days refer to the days after a fresh NB solution (day-1) was placed in the reservoir. For instance, the time point for the 100% solution on the 5th day corresponds to the size and concentration of the initial NB solution that was left in the reservoir after 5 days. Then, the 75%, 50%, and 25% solutions were prepared by diluting this solution and measured before and after boiling on the same day. From a numerical perspective, it is noted that Table 1 presents the results of the 5th day.

During boiling, water bubbles are formed. If the radius of these bubbles is R_w, their terminal velocity of increase (U) will be

$$U = \frac{g}{3} \times \frac{\rho}{\mu} \times R_w^2, \qquad (1)$$

where ρ and μ are the density and viscosity of water near 100 ºC, respectively, and g is the acceleration of gravity. The Reynolds number (Re) is then equal to

$$\mathrm{Re} = \frac{2R_w U \rho}{\mu}, \qquad (2)$$

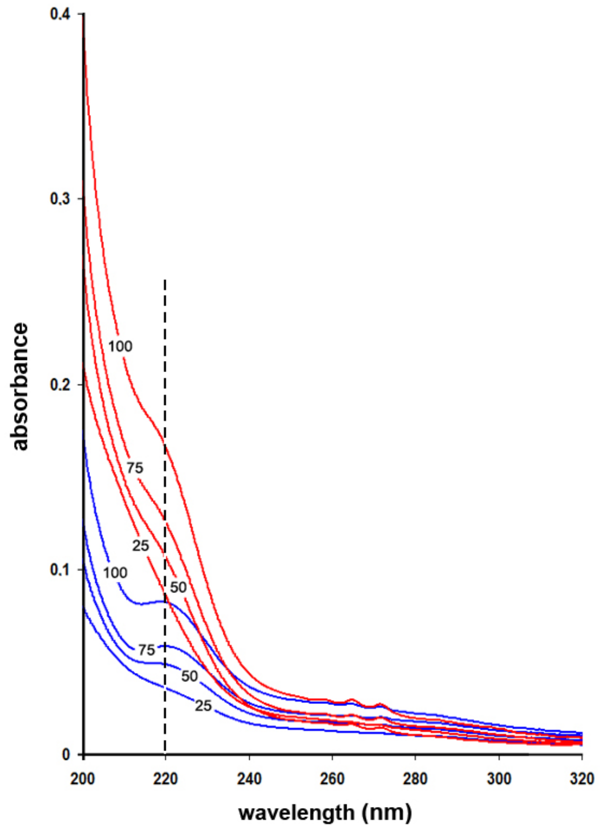

Fig. 2. UV absorption spectra of a NB solution at different dilutions. Blue lines: before boiling; red lines: after boiling; numbers on the spectra lines: % of dilution. The broken line shows where the peak and the hump are located.

For a rising bubble of radius 0.8 mm, Re=400. This value suggests that the bubble moves along a spiraling course that is influenced by the same wake conditions [41-42]. Nanobubbles in water are negatively charged [43]; the zeta potential of NBs in DI water is reported to be about -65 mV [44].

Water bubbles are also negatively charged but much larger than bNBs [45]. On their way to the surface, they repel bNBs by their wake. As a result, bNBs are not dragged on the surface by the rising water bubbles and thus are prevented from bursting. Figure 4 depicts this mechanism.

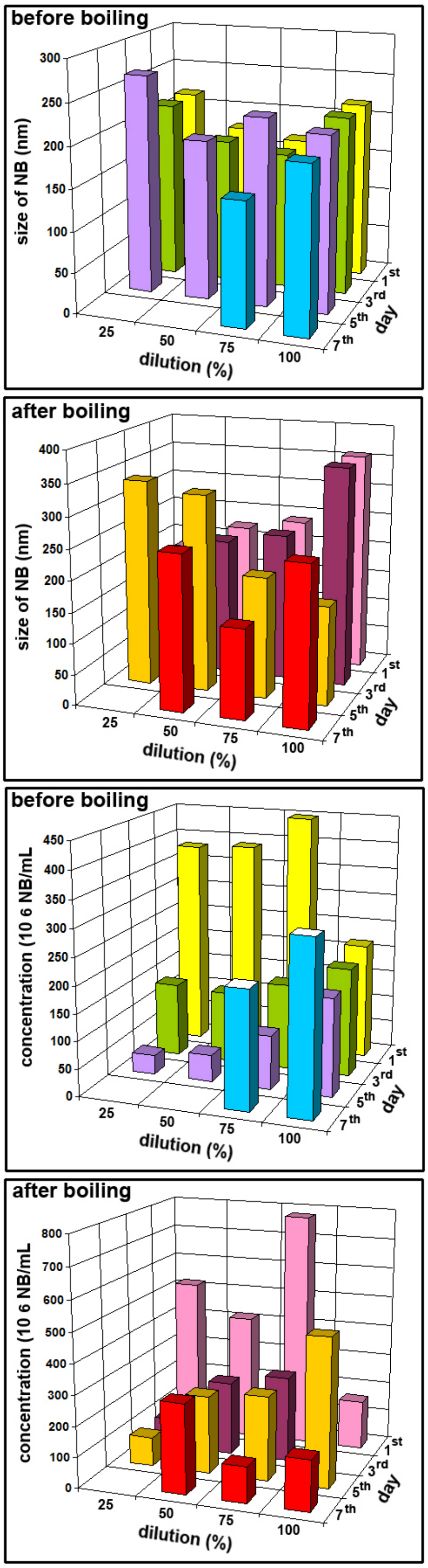

Fig. 3. Size and concentration of NBs before and after boiling over a time span of 7 days (see text for details).

Boiling does not seem to increase the population of NBs per se, because if there was such an increase, the population of NBs would be about the same for all solutions. Furthermore, NBs do not change the boiling point of water, indicating that NBs do not rise above vapor bubbles (Figure 5); possibly, they speed up the boiling process. During boiling, the rupture of liquid often occurs at the walls of the vessel [46] where sNBs reside.

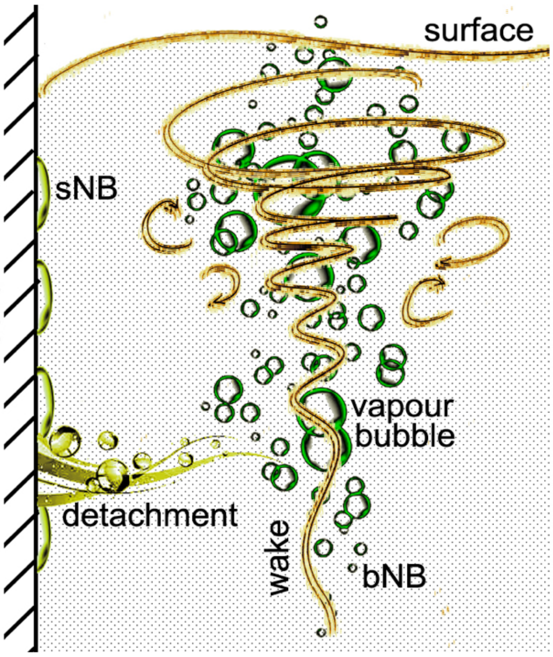

Fig. 4. Mechanism of NB survival from boiling.

Since boiling is an endothermic process, the sNB→bNB direction will be favoured. As temperature rises, sNBs, become detached from the walls to the bulk, causing an increase in their concentration. To investigate these hypotheses further, we i) measured DI water (i.e., without NB) after boiling, ii) revisited the results of the 5th day, and iii) re-examined the post-boil solution from that day 12 days later without re-boiling it. Figure 6 shows the results.

After boiling, DI water gains a low concentration of MBs (10.3×10^6 MB/mL) with mean radius of ~1 μm (Figure 6a). This indicates that boiling, per se, does not generate NB, as was assumed in the previous paragraph.

Before boiling the 100% nominal solution showed a concentration of 182×10^6 NB/mL with a mean size of 215 nm (Figure 6b). After boiling the concentration increased to 487×10^6 NB/mL, and the size decreased to 161 nm (Figure 6c). During boiling, water bubbles eject sNBs from the vessel walls, and these collide with the bulk of the solution, producing various random sizes of NBs (see Figure 4): averagely larger, smaller, or equal to the mean size of the acting bNBs. As a result, the population of bNBs increases, and in this particular case under investigation, their size decreased. After 12 days, it was found that the concentration decreased to 312×10^6 NB/mL, and the size increased to 291 nm (Figure 6d).

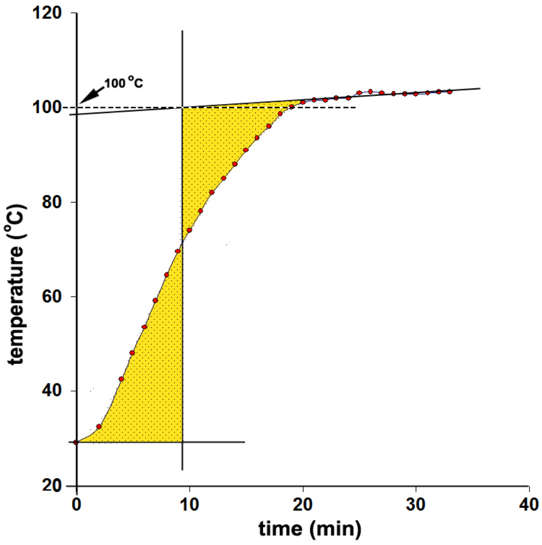

Fig. 5. Thermogram for the boiling point of DI water with 100% NB; yellow areas are equal.

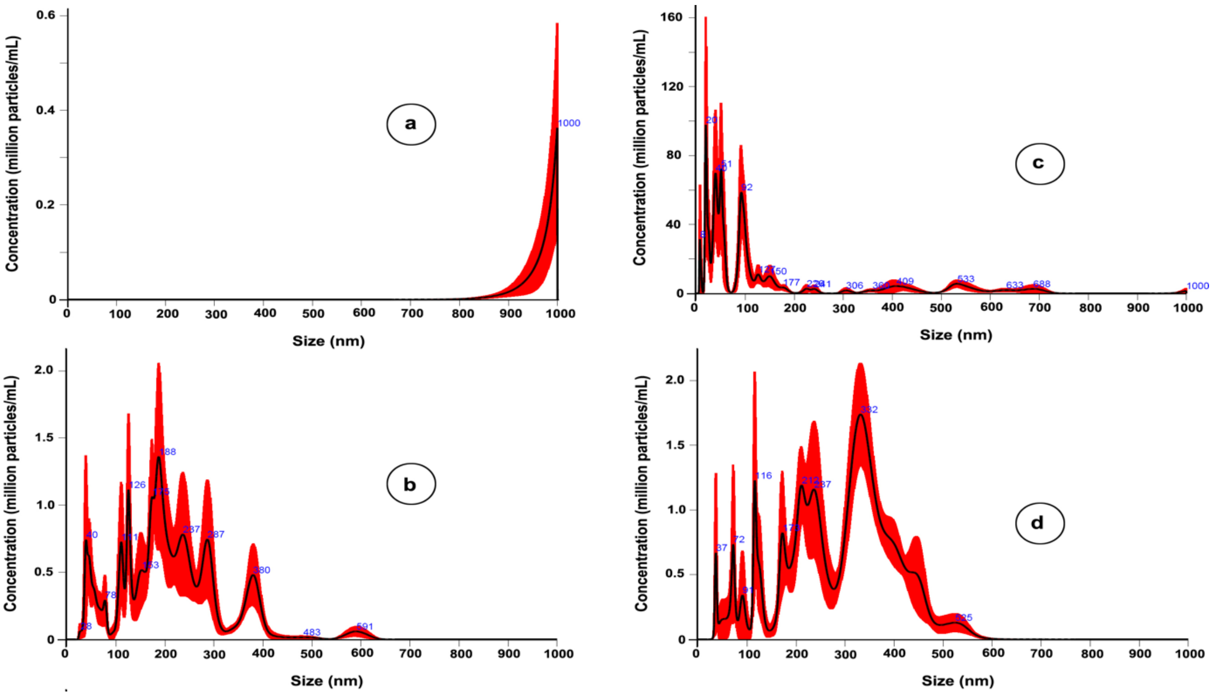

Fig. 6. Concentration of NB against their sizes. a) DI water after boiling (no NB, only a small concentration of MB appears); b) DI water with 100% NB before boiling; c) the same as in case (b) solution after boiling; and d) the same as in case (c) solution after 12 days without boiling. Errors are indicated in red bars.

The decrease in concentration was theoretically expected, as already discussed, and may also be due to a reverse course of events. Small bNBs, having greater Brownian motion, turn into sNBs by moving towards the vessel walls; thus, the mean size of the remaining bNB increases.

4. Conclusions

The effect of the dilution and boiling of aqua solutions containing NBs was examined. Dilution led to a lower concentration of NBs than expected, indicating a possible exchange from bNBs to sNBs, with the latter not contributing to the measured populations. Boiling, on the other hand, caused an increase in the concentration of NBs that was higher than expected. As a general trend, in most cases, the population of NBs decreased with dilution. However, the standard errors for the dilution process are smaller than those for boiling. Although the boiling of a liquid is considered a well-studied process there are still several mysteries to be understood [47], one reason being the chaotic nature of the process induced by the difficulty associated with uniformly changing the temperature.

The results collected before and after boiling changed from sample to sample and time to time. To this end, we constructed 3D charts to visualize the changes in both the size and concentration of NBs. The change in size was scattered randomly but not drastically, whereas the concentration mostly decayed with dilution. We propose a mechanism of how NBs survive boiling and how their population increases and their sizes change by suggesting an exchange from sNBs to bNBs and vice versa. By boiling DI water, it was concluded that boiling produces MBs, not NBs. By re-examining a boiled solution after 12 days, it was found that concentration and size decreased. Further study in this direction is underway to examine the effects of heating and boiling over time.

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