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Nucleation stage with nonsteady growth of supercritical gas bubbles in a strongly supersaturated liquid solution and the effect of excluded volume

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An approach to the kinetics of barrier formation of supercritical gas bubbles in a strongly supersaturated liquid solution is presented. A common assumption of uniform reduction of a dissolved gas supersaturation in a liquid solution via stationary diffusion to nucleating gas bubbles is shown to be not applicable to the case of high gas supersaturations. The approach recognizes that the diffusion growth of supercritical bubbles at high gas supersaturation is essentially nonstationary. Nonstationary growth of an individual gas bubble is described by a self-similar solution of the diffusion equation which predicts a renormalized growth rate and thin highly nonuniform diffusion layer around the bubble. The depletion of a dissolved gas due to intake of gas molecules by the bubble occurs only within this thin layer. An integral equation for the total volume of an ensemble of supercritical gas bubbles within a liquid solution is derived. This equation describes the effect of excluding a total volume of the depleted diffusion layers around the growing bubbles nucleated at all previous moments of time until nucleation of new bubbles ceases due to elimination of the nondepleted volume of the solution. An analytical solution of this equation is found. The swelling of the liquid solution, the number of gas bubbles nucleated, the distribution function of bubbles in their sizes, and the mean radius of the bubbles are determined in their dependence on time.

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I. INTRODUCTION

Formation of gas bubbles in supersaturated-with-gas liquid solutions (degassing) is a well spread event both in natural and technical processes. This phenomenon can be desirable or undesirable from a practical point of view; in any case it drastically changes material properties and affects the character of gas-liquid decomposition. Therefore prognostication and controlling the bubble formation at desorption of dissolved gases are very important. A control of generation intensity and growth rate of gas bubbles is needed not only at production of carbonated beverages, but at molding of porous materials and polymer foams [1], at glass formation [2], at casting and aging of metals and ceramics [3], and at investigation of decompression sickness caused by gas bubbles in human blood and tissue under decompression [4]. The kinetic theory of nucleation and growth of the bubbles of water vapor dissolved in magma melt would allow us to describe a swelling process leading to explosive volcanic eruptions [5,6].

This paper presents a theoretical approach to kinetics of gas bubble formation in a liquid solution under high initial supersaturation of the solution by a dissolved gas. Only at strong gas supersaturations, the gas bubble formation itself can be observed with a noticeable intensity on the nucleation stage, i.e., the stage which continues until the generation of new supercritical bubbles ceases. Considering the strong supersaturations, we will assume that they are not close to the solution spinodal so that nucleation of critical bubbles still requires an overcoming a certain activation barrier. The arguments we present here do not touch the initial (incubation) stage of the bubble formation where the steady nucleation rate is formed [7,8].

It is usually presumed in the conventional approach to the kinetics of decomposition of a supersaturated solution into liquid and gas phases, that uptake of gas molecules by growing bubbles brings synchronous and uniform (for the whole solution) reduction of the solution gas supersaturation [9–14]. It means that the solution is considered to be an effectively uniform environment where an initial excess of a dissolved gas diminishes in time due to gathering gas molecules in the bubbles. This process is accompanied by uniform-in-volume reduction of the intensity of generation of new supercritical bubbles. Because the intensity of generation of supercritical bubbles is very sensitive to the supersaturation degree, the generation of new bubbles practically stops at relatively small decrease of the uniform-in-volume gas supersaturation (if compared with an initial value of the supersaturation). As a result within these frameworks, when the nucleation stage is completed, almost the whole gas still stays dissolved in the liquid, and the main part of the dissolved gas excess comes into growing bubbles only on the next stage of the bubble growth. The total number of growing bubbles stays unchanged until the Lifshitz-Slezov [15,16] stage. This situation is similar to that in the kinetics of droplet nucleation in closed systems under ballistic or diffusion regime of growth [17–20].

It should be noted that the applicability of the concept of the uniform supersaturation is valid only when the sizes of diffusion shells surrounding the bubbles are large in comparison with not only the sizes of the bubbles themselves but with the mean distance between the bubbles. The concept assumes that the diffusion shells contain many neighbor bubbles. Such a situation is by no means always the case. For instance, it is not the case at the very beginning of nucleation

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process when the total number and sizes of the bubbles are so small that the mean distance between the bubbles is many times larger than the radii of the bubbles and their diffusion shells.

Indeed, each bubble "knows" nothing about its neighbors while the diffusion shells of separate bubbles stay nonoverlapped. The local supersaturations of solution diminish significantly only within the diffusion shells around the bubbles and do not change beyond the shells. Thus the growth rate of each bubble is determined on this stage by an initial value of solution bulk supersaturation. Along with that, generation of new supercritical bubbles per unit volume is practically damped within the diffusion shells and keeps its initial rate beyond the shells. Because the number of bubbles and the volume of the bubbles and diffusion shells grow in time, the formation of new stably growing embryos of new phase slows down due to the effect of excluded volume, i.e., decreasing the solution volume available for an intensive bubble nucleation. The nucleation stage continues in this case until the intensity of new bubble formation ceases due to elimination of the nondepleted-in-gas volume of the solution.

The theory of the effect of excluded volume on the nucleation stage will be given in this paper on the basis of derivation and solution of integral equation for the time evolution of the total volume of the ensemble of gas bubbles in liquid solution. This equation will be derived with excluding a total volume of depleted nonstationary diffusion layers around the growing bubbles nucleated at all previous moments of time. Using the solution of this equation, we will show how the gas-liquid solution swells and how the number of gas bubbles nucleated, the distribution function of bubbles in their sizes, and the average radius of the bubbles can be determined in their dependence on time on the stage of nucleation.

We will not consider here any next stage of bubble formation, including the Lifshitz-Slezov stage, though they can be also influenced by the effect of excluded volume. This question requires a special study. It should also be noted that the effect of excluded volume has no relation with the finite system effects on vapor nucleation at strong supersaturations studied in Refs. [21–23].

II. FAILURE OF THE STATIONARY DIFFUSION APPROXIMATION IN A STRONGLY SUPERSATURATED SOLUTION

Process of formation of supercritical bubbles on nucleation stage depends essentially on the relation between the sizes of growing bubbles and surrounding these bubbles diffusion shells. Such a relation is determined by the initial gas supersaturation of solution. We consider this question below in detail with qualitative estimates.

Let state of solution be determined by temperature T, pressure Π and initial value of number density n_0 of the dissolved gas molecules in the solution. We denote as n_∞ the value of number density of dissolved gas molecules in saturated solution being in thermal, chemical and mechanical equilibrium at the temperature T and the pressure Π with the same pure gas at flat interface of their contact. The quantity $(n_0-n_\infty)/n_\infty$ is the solution supersaturation. This quantity is much larger than unity, and, consequently, $n_0 \gg n_\infty$.

Assuming the nucleating bubbles to be spherical, we will consider the bubble radius R to be sufficiently large to provide a strong inequality

$$R \gg \frac{2\sigma}{\Pi} \tag{1}$$

where σ is the surface tension of the liquid solvent. Inequality (1) can be applied to description of a bubble ensemble if it fulfils for an average (over the ensemble) bubble radius. Due to inequality (1), the influence of the capillary pressure is very small, and the gas pressure within the bubble, at its mechanical equilibrium with the solution, is equal to the solution pressure Π. Under the same conditions, the gas in the bubble can be considered ideal. As a result, we have the following relation for number density n_g of gas molecules in the bubble at thermal equilibrium with the solution,

$$n_g = \Pi/kT \tag{2}$$

where k is the Boltzmann constant.

If the initial excess concentration n_0-n_∞ of gas molecules in the solution is small in comparison with their concentration n_g in the bubble, then filling the bubble with the gas can be provided by the diffusion influx of gas molecules out the diffusion shell which size is much larger than the size of the bubble itself. As a result, the diffusion flux will be close to the stationary state, and the bubble growth be slow, obeying the differential equation $d(4\pi/3)n_gR^3/dt=4\pi RD(n_0-n_\infty)$ where D is the diffusion coefficient of the gas molecules in the liquid solvent and t is the time. We can qualitatively write in this case the balance of gas molecules coming into a bubble out of diffusion shell in the form

$$(4\pi/3)n_gR^3 \simeq \alpha(n_0-n_\infty)4\pi RDt \tag{3}$$

where α is an adjusting numerical coefficient of order of unity. Time t is counted here off the moment of fluctuation appearance of the supercritical bubble growing irreversibly. Equation (3) gives

$$R \approx (3\alpha a)^{1/2}(Dt)^{1/2} \tag{4}$$

for the dependence of the bubble radius on time, where the dimensionless parameter a is defined as

$$a \equiv \frac{n_0-n_\infty}{n_g}. \tag{5}$$

The inequality $R \ll (Dt)^{1/2}$ implying that the size of the diffusion shell (which is of order of the diffusion length $(Dt)^{1/2}$) is large in comparison with the bubble size, is the condition of diffusion mixing of the solution and is actually equivalent to inequality $a^{1/2} \ll 1$. Thus one may expect that the approximation of uniform-in-volume depletion of gas supersaturation is applicable only at the limit of small values of the parameter a.

The parameter a has a simple physical meaning. We can clarify this meaning using the condition of conservation of the total number of gas molecules in the solution in the form

$$n_g V_{gf} = (n_0 - n_\infty) V_l \tag{6}$$

where V_l is the volume of liquid solvent, and V_{gf} is a final sum of volumes of gas bubbles formed as a result of complete intake of an initial supersaturation excess of gas dissolved. Taking into account Eq. (5) and introducing notation V_f for the total final volume of the solution, we rewrite condition (6) as

$$V_f = V_l + V_{gf} = (1 + a) V_l. \tag{7}$$

Thus, due to formation of gas bubbles, the final volume of solution increases $1+a$ times in comparison with its initial volume. This shows the meaning of the parameter a as a degree of a liquid-gas solution swelling at degassing.

Because, as was shown above, the approximation of uniform-in-volume depletion of gas supersaturation is valid only at $a^{1/2} \ll 1$, then it follows from Eq. (7) that all the results obtained within this approximation are applicable only in the cases when the total volume of solution swells to a little degree at desorption of a dissolved gas.

The excess concentration $n_0 - n_\infty$ of gas molecules in a solution is large in comparison with the gas concentration n_g within a growing bubble in the case of strong initial supersaturation of the solution. Thus, in view of Eq. (5), inequality $a \gg 1$ is fulfilled. In this case, a diffusion influx of gas molecules out of thin (in comparison with the bubble radius) layer of the surrounding solution is sufficient for filling a bubble. Recognizing that the thickness of this layer is of order of the diffusion length $(Dt)^{1/2}$, one can estimate the number of gas molecules coming from the layer to the bubble in the form

$$(4\pi/3) n_g R^3 \simeq \beta (n_0 - n_\infty) 4\pi R^2 (Dt)^{1/2}, \tag{8}$$

where β is an adjusting numerical coefficient of order of unity. It follows from Eq. (8)

$$R \approx 3\beta a (Dt)^{1/2}. \tag{9}$$

In view of strong inequality $a \gg 1$, Eq. (9) yields $R \gg (Dt)^{1/2}$. Thus a thickness of the diffusion shell with nonuniform concentration of solution around a bubble is really small in comparison with the bubble radius. As a consequence, the approximation of uniform-in-volume depletion of supersaturation of solution is absolutely unsuitable for description of the nucleation stage of bubble formation at strong initial gas supersaturations.

Now we can say that the most realistic picture of the nucleation stage in a strong supersaturated liquid-gas solution is one where a local intensity of bubble nucleation is highly nonuniform in space. The nucleation of new supercritical bubbles is practically damped within thin diffusion shells with dropping gas concentration around the growing bubbles. Along with that, the gas concentration (and, correspondingly, the intensity of nucleation of new bubbles) keeps practically its initial value outside the shells. Under such conditions, formation of new stably growing embryos of new phase is slowed down not by uniform in volume decreasing the gas supersaturation, but by monotonic reducing (due to growth of old and nucleation of new bubbles) the solution volume available for an intensive nucleation. The ability of nucleation of new growing bubbles is maintained until the moment when the diffusion shells around the bubbles spread over the whole liquid solvent.

The another approach using the idea of excluded volume for a description of the nucleation stage of gas bubble formation under conditions of decompression of the gas-saturated melt was recently proposed in [24]. Let us note that there are several shortcomings in this approach. First of all, this approach applies the concepts and conclusions of the Kolmogorov theory [25] of crystallization of an immobile melt with point embryos to the situation with movable liquid solution around growing gas bubbles. Besides, this approach uses the approximation of stationary diffusion growth of nucleating bubbles. As is clear from that said above, this approximation is incorrect under the condition $a \gg 1$ of strong supersaturation of a solution. Another application of the idea of excluded volume has been recently developed in [26,27] for a problem of crystallization of undercooled melt. We will return to the approach from [26,27] in the next section.

III. INTEGRAL EQUATION FOR THE TOTAL VOLUME OF GAS BUBBLES

To determine rigorously a volume of the diffusion shell which surrounds a gas bubble in a liquid solution and where nucleation of new bubbles is damped, one can use the results of the self-similar theory of isothermal nonsteady diffusion growth of a bubble with account of motion of the liquid solvent due to the bubble growth [28]. This theory gives for the dependence of a supercritical bubble radius on time t the following expression

$$R = (2bDt)^{1/2} \tag{10}$$

where time is counted off from the moment of appearance of the supercritical bubble, and the dimensionless parameter b is linked to the previously determined parameter a as [28]

$$\frac{a}{b} = \int_1^\infty \frac{dx}{x^2} e^{-bx^2/2 - b/x + 3b/2}. \tag{11}$$

A solution of Eq. (11) with respect to b can be rather easily found in two limiting cases at $a^{1/2} \ll 1$ and $a \geq 10$. It follows from Eq. (11) in the case $a^{1/2} \ll 1$ that $b \approx a$, and Eq. (10) is reduced to Eq. (4) at $\alpha = 2/3$. This is the case when diffusion of gas molecules to a bubble is close to a stationary process [28]. The case $a \geq 10$ corresponds to a strong initial supersaturation of solution, and Eq. (11) gives at this

$$b \approx \frac{6}{\pi} a^2. \tag{12}$$

This is the case of essentially nonsteady diffusion of gas molecules to a bubble [28]. Now Eq. (10) is reduced to Eq. (9) at $\beta = (4/3\pi)^{1/2}$. Both these results confirm the qualitative estimates obtained in the section II for the relation between radius R of a growing supercritical bubble and the diffusion length $(Dt)^{1/2}$ at $a^{1/2} \ll 1$ and $a \gg 1$.

It has been shown in [28] that the isothermal character of the bubble growth, the diluteness of the liquid solution and mechanical equilibrium of the bubble with the solution (which are used in our approach here) can be provided (at least for water solutions) at $a \leq 18$. This allows us to consider the case $a \geq 10$ to be realized within the rather wide range $10 \leq a \leq 18$.

As was rigorously shown in [29] in the frameworks of the self-similar theory of isothermal nonsteady diffusion growth of a bubble at $a \geq 10$, the concentration of a dissolved gas outside the sphere with radius $R(1+1/a)$ centered at the center of the bubble coincides with a high accuracy with the initial gas concentration n_0. The concentration of a dissolved gas on the sphere with radius R (at the surface of the bubble) is equal to the concentration n_∞ of saturated solution which is much smaller than concentration n_0 at large supersaturation $(n_0 - n_\infty)/n_\infty$. This shows a high nonuniformity of the diffusion layer around the growing bubble at $a \geq 10$, and one can set the thickness of the diffusion shell around the bubble with radius R, where nucleation of new growing embryos is damped due to depletion of gas, as equal to R/a. Correspondingly, the volume of this shell, that should be excluded from the solution volume available for nucleation, equals at $a \geq 10$,

$$V_{ex}(R) = \frac{4\pi}{3}((1 + 1/a)^3 - 1)R^3 \approx \frac{4\pi}{a}R^3. \qquad (13)$$

The ratio q of the excluded volume $V_{ex}(R)$ to the volume

$$V_R(t) = \frac{4\pi}{3}R^3(t) \qquad (14)$$

of a growing bubble with radius $R(t)$ equals

$$q \equiv V_{ex}(R)/V_R(t) = 3/a. \qquad (15)$$

Because the quantity q does not depend on bubble radius, the same ratio is valid for every growing bubble in solution, i.e., for the whole ensemble of supercritical bubbles. In other words, if the total volume of bubbles in time moment t is $V_g(t)$, then nucleation of new bubbles is damped within the part of a liquid solution with volume $qV_g(t)$. Correspondingly, an initial intensity of nucleation preserves in volume $V_1(t)$ determined as

$$V_1(t) = V_l - qV_g(t) \qquad (16)$$

where the volume V_l of a liquid solvent (which is constant in time) can be considered as the initial volume of the liquid solution. Thus the quantity $qV_g(t)$ has a meaning of the total excluded volume of highly nonuniform nonstationary diffusion layers around all growing bubbles nucleated to the time moment t.

The number $dN(\tau)$ of bubbles nucleated in solution for a small interval of time from moment τ to moment $\tau + d\tau$ equals

$$dN(\tau) = IV_1(\tau)d\tau = I(V_l - qV_g(\tau))d\tau \qquad (17)$$

where I is the intensity of nucleation (the nucleation rate) of growing supercritical bubbles per unit of time and per unit of solution volume at initial gas supersaturation. Setting the radius of bubbles at moment of nucleation to be equal to zero, and using Eq. (10) for the radius of growing bubble, we obtain with the help of Eq. (17) the following integral equation for the total volume $V_g(t)$ of growing bubbles in time moment t

$$V_g(t) = I\int_0^t d\tau (V_l - qV_g(\tau))V_R(t-\tau). \qquad (18)$$

The volume $V_R(t-\tau)$ of a single bubble in the integrand is determined by Eqs. (10) and (14) in all preceding time moments. Integral Eq. (18) formally coincides with Eq. (2) from [26] and Eq. (15) from [27]. However function $V_R(t-\tau)$ in our case is a fractional power function of time, and this determines quite different from [26,27] way of analysis of Eq. (18).

Let us introduce the quantity

$$y \equiv V_g(t)/V_l \qquad (19)$$

which is the total volume of growing bubbles in terms of initial volume V_l. Using Eqs. (19), (10), and (14), Eq. (18) can be rewritten as

$$y(t) = \lambda t^{5/2}\int_0^1 ds(1-s)^{3/2}[1 - qy(ts)] \qquad (20)$$

where

$$\lambda \equiv \frac{4\pi}{3}I(2Db)^{3/2}. \qquad (21)$$

It is more convenient to work with function

$$z(t) \equiv V_1(t)/V_l, \quad z(t) = 1 - qy(t) \qquad (22)$$

[we used Eqs. (16) and (19)]. Expressing $y(t)$ through $z(t)$ with the help of Eq. (22) in Eq. (20), we obtain an integral equation for $z(t)$,

$$z(t) = 1 - q\lambda t^{5/2}\int_0^1 ds(1-s)^{3/2}z(ts). \qquad (23)$$

Function z has a meaning of the volume fraction of a liquid solvent where nucleation rate maintains on an initial level. This function is positive and monotonically decreases from unity at the beginning to zero at the end of nucleation stage.

IV. CHARACTERISTICS OF ENSEMBLE OF GROWING BUBBLES ON THE NUCLEATION STAGE

As is shown in Appendix, the exact solution of Eq. (23) can be found in the form of power series. As a result we have

$$z(t) = \sum_{k=0}^{\infty}(-1)^k\frac{(q\lambda\Gamma(5/2)t^{5/2})^k}{\Gamma(5k/2+1)}. \qquad (24)$$

The required non-negativity of function $z(t)$ preserves for time interval $0 \leq t \leq t_1$ where t_1 is the smallest positive root of function z determined by power series (24). The time moment $t = t_1$ corresponds to the end of nucleation stage. Thus the duration of nucleation stage can be found as solution of equation

$$z(t_1) = 0. \qquad (25)$$

Recognizing that convergence of series (24) is fast, we can keep in series (24) for determination of time t_1 only two first terms. Using for $z(t)$ the approximation

$$z(t) = 1 - (2/5)q\lambda t^{5/2} \tag{26}$$

and substituting Eq. (26) into Eq. (25) yields

$$t_1 = \left(\frac{5}{2q\lambda}\right)^{2/5} \tag{27}$$

(quantities q and λ are defined by Eqs. (15) and (21)). Using the explicit relations for the coefficients in series (24) and recognizing that these series are alternating, it is not difficult to show that relative error of t_1 value given by Eq. (27) is already sufficiently small and approximately equals $5\cdot 10^{-2}$. Therefore we will use in subsequent estimates approximations (26) and (27).

As follows from Eqs. (22), (26), and (27),

$$V_1(t) = V_l(1 - (t/t_1)^{5/2}). \tag{28}$$

In view of Eqs. (16), (22), and (28), the total volume of bubbles increases in time as

$$V_g(t) = \frac{V_l}{q}[1 - z(t)] = \frac{V_l}{q}(t/t_1)^{5/2} \tag{29}$$

and achieves to the end of nucleation stage the value

$$V_g(t_1) = \frac{V_l}{q} = \frac{a}{3}V_l \tag{30}$$

[we used Eq. (15)]. At this the volume of the whole solution increases to the value

$$V(t_1) = V_l + V_g(t_1) = \left(1 + \frac{a}{3}\right)V_l. \tag{31}$$

This rise is significant at $a \geq 10$, although, in view of Eq. (7), $V(t_1)$ equals approximately one third of V_f.

The total number $N(t)$ of gas bubbles in solution depends on time according to Eqs. (17) and (28) as

$$N(t) = I\int_0^t V_1(\tau)d\tau = IV_l t\left(1 - \frac{2}{7}(t/t_1)^{5/2}\right). \tag{32}$$

The total number of supercritical bubbles at the end of nucleation stage equals

$$N(t_1) = \frac{5}{7}IV_l t_1. \tag{33}$$

Using Eqs. (10) and (28), let us rewrite integral relation (32) with changing the integration variable τ by variable $t - t'$ [t' is the time of droplet growth from zero radius at the beginning to radius $R' = R(t')$]. Using again Eq. (10), we pass in the integrand for $N(t)$ from integration over t' to integration over R'^2. As a result we have

$$N(t) = \frac{IV_l}{2Db}\int_0^{2Dbt} dR'^2\left[1 - \frac{(t - R'^2/(2Db))^{5/2}}{t_1^{5/2}}\right]. \tag{34}$$

It follows from Eq. (34) that distribution of bubbles in variable R^2 at current moment of time t and at $R^2 < 2Dbt$ (where this distribution just differs from zero) is given as

$$N(R^2,t) = \frac{IV_l}{2Db}\left[1 - \frac{(t - R^2/(2Db))^{5/2}}{t_1^{5/2}}\right]. \tag{35}$$

The mean bubble radius $\bar{R}(t)$ at time moment t can be found with the help of Eq. (35) as

$$\bar{R}(t) \equiv \frac{1}{N(t)}\int_0^{2Dbt} dR^2 RN(R^2,t) = \frac{2}{3}R(t)\frac{1 - \frac{15\pi}{256}(t/t_1)^{5/2}}{1 - \frac{2}{7}(t/t_1)^{5/2}} \tag{36}$$

where radius $R(t)$ is defined by Eq. (10) and corresponds to the largest bubble at this moment of time. In particular, Eq. (36) gives at the time moment t_1 at the end of nucleation stage: $\bar{R}(t_1) \approx 0.76R(t_1) = 0.76(2Dbt_1)^{1/2}$.

Using Eqs. (12), (15), and (21), let us rewrite Eq. (27) for time t_1 of nucleation stage in the form

$$t_1 \simeq \left(\frac{5}{8}\right)^{2/5}\left(\frac{1}{12}\right)^{3/5}\frac{\pi^{1/5}}{I^{2/5}D^{3/5}a^{4/5}}. \tag{37}$$

Substituting Eq. (37) in Eq. (33) yields

$$N(t_1) \simeq \frac{5}{7}\left(\frac{5}{8}\right)^{2/5}\left(\frac{1}{12}\right)^{3/5}\frac{\pi^{1/5}V_l I^{3/5}}{D^{3/5}a^{4/5}}. \tag{38}$$

One can see from Eqs. (37) and (38) that time t_1 does not depend on V_l, and the total bubble number $N(t_1)$ is proportional to V_l.

Formula (10) assumes that self-similar growth of supercritical bubble starts since its nucleation. It fulfils if the bubble radius is so large that strong inequality (1) is valid with a reserve. Therefore we define a characteristic radius R_D starting from which Eq. (10) is applicable to the bubble growth as

$$R_D \sim 40\sigma/\Pi. \tag{39}$$

Equation (18) holds at

$$\bar{R}(t_1)/R_D \gg 1. \tag{40}$$

To check inequality (40), we need some numerical estimates for $\bar{R}(t_1)$ and R_D. It follows from Eq. (36) with account of Eqs. (10), (12), and (37) that

$$\bar{R}(t_1) \sim \frac{D^{1/5}a^{3/5}}{I^{1/5}}. \tag{41}$$

One can see that dependence of $\bar{R}(t_1)$ on D and I is rather weak. We can use for the parameters in Eqs. (39) and (41) when water is a liquid solvent the following values:

$$\sigma \simeq 75 \text{ mJ m}^{-2}, \quad D \simeq 1.6\cdot 10^{-9} \text{ m}^2/\text{c}, \quad \Pi = 10^5 \text{ Pa}. \tag{42}$$

The values of nucleation rate I lie at $a \geq 10$ in the interval $I \sim 10^6 - 10^{11}$ m^{-3} c^{-1}. Using Eqs. (39) and (41) with account of Eq. (42) and estimation of I, one can see that strong inequality (40) indeed is fulfilled at $a \geq 10$.

V. SUMMARY

Let us now summarize which important facts have been revealed by the analysis presented in this paper. It was shown that behavior of an ensemble of gas bubbles at nucleation stage under high gas supersaturation in a liquid containing dissolved gas can be described with the help of solution of integral Eq. (18) for the total volume of growing gas bubbles. Equation (18) [and its representations given by Eqs. (20) and (23)] takes into account the effect of excluding a volume of highly nonuniform nonstationary diffusion layers around the growing bubbles nucleating at all previous moments of time. Nucleation rate entering Eq. (18) refers to the initial high gas supersaturation of a liquid-gas solution. The available volume of solution, the total volume of bubbles nucleated, the number of gas bubbles, the distribution function of bubbles in their sizes, and the mean radius of the bubbles are determined in their dependence on time by Eqs. (28), (29), (32), (35), and (36), respectively. The duration of nucleation stage and the final values of the total volume of solution and the total number of gas bubbles nucleated at the end of nucleation stage are given by Eqs. (37), (31), and (38).

Let us note that power indices of dimensional quantities I, D, and V_l in Eqs. (37), (38), and (41) for the time t_1 of nucleation stage and the total number $N(t_1)$ and the mean radius $\bar{R}(t_1)$ of gas bubbles are determined by scale relations providing the correct dimensionalities of the quantities t_1, $N(t_1)$, and $\bar{R}(t_1)$. From that point, these indices are just the same as the indices for a theory assuming a uniform uptake of a dissolved gas from the liquid solution via stationary diffusion to gas bubbles [9,10] or Kolmogorov-like theory [24]. It was shown however that latter theories cannot be applied to the most interesting case of high initial supersaturations and nucleation rates. The most important difference in predictions of our approach and the theory with uniform-in-volume depletion is a possibility of description of far large swelling of a liquid-gas solution at its degassing.

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APPENDIX: SOLUTION OF INTEGRAL EQUATION

Let us consider integral equation in the form

$$f(t) = 1 - \gamma \int_0^t dt_1 (t - t_1)^n f(t_1) \tag{A1}$$

where $n > -1$. Introducing new integration variable $s = t_1/t$, we rewrite Eq. (A1) in the form

$$f(t) = 1 - \gamma t^{n+1} \int_0^1 ds (1 - s)^n f(ts). \tag{A2}$$

With method of subsequent iterations, Eq. (A2) can be solved in the form of power series. It is evident that these series will contain only powers of t^{n+1}. Therefore it convenient to pass in function f to a new argument $u = t^{n+1}$. Equation (A2) is transformed at this as

$$f_1(u) = 1 - \gamma u \int_0^1 ds (1 - s)^n f_1(s^{n+1} u) \tag{A3}$$

where $f_1(u) \equiv f[t(u)]$.

We will seek a solution of Eq. (A3) in the form of power series

$$f_1(u) = \sum_{k=0}^{\infty} a_k u^k. \tag{A4}$$

It follows from Eqs. (A3) and (A4) that $a_0 = 1$. Then, because

$$a_k = f_1^{(k)}(0)/k\,!\,, \tag{A5}$$

the following relation takes place at $k \geq 0$:

$$a_{k+1}/a_k = \frac{1}{k+1} f_1^{(k+1)}(0)/f_1^{(k)}(0). \tag{A6}$$

To find a ratio of derivatives on the right-hand side of Eq. (A6), we will differentiate $k+1$ times both sides of Eq. (A3) with respect to u and set $u = 0$. As a result we have

$$f_1^{(k+1)}(0) = - \gamma (k+1) f_1^{(k)}(0) \int_0^1 ds (1 - s)^n s^{(n+1)k}. \tag{A7}$$

An integral on the right-hand side of Eq. (A7) represents beta function and can be expressed through Γ functions as

$$\int_0^1 (1 - s)^n s^{(n+1)k} ds = \frac{\Gamma(n+1)\Gamma[(n+1)k+1]}{\Gamma[(n+1)(k+1)+1]}. \tag{A8}$$

Using Eqs. (A7) and (A8), we find from Eq. (A6)

$$a_{k+1}/a_k = - \gamma \frac{\Gamma(n+1)\Gamma[(n+1)k+1]}{\Gamma[(n+1)(k+1)+1]}. \tag{A9}$$

A unique consequence of the coefficients a_k which satisfies to condition $a_0 = 1$ and Eq. (A9) at $k \geq 0$ is determined by formula

$$a_k = (-1)^k \frac{[\gamma \Gamma(n+1)]^k}{\Gamma[(n+1)k+1]}. \tag{A10}$$

Substituting Eq. (A10) in Eq. (A4) and passing back to variable t, we find the following expression for function $f(t)$:

$$f(t) = \sum_{k=0}^{\infty} (-1)^k \frac{[\gamma \Gamma(n+1) t^{n+1}]^k}{\Gamma[(n+1)k+1]}. \tag{A11}$$

With setting $\gamma = \lambda q$, $n = 3/2$, and $f(t) \equiv z(t)$, Eq. (A2) coincides with Eq. (23). This shows that a function determined by power series (24) indeed is a solution of Eq. (23).

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