Bubbstons: stable microscopic gas bubbles in very dilute electrolytic solutions

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Theoretical results derived here point to the existence of stable microscopic gas bubbles (bubbstons) in solutions consisting of a liquid, a gas, and a small electrolyte impurity. The radius of the bubbstons is found as a function of the properties of the solution. The spontaneous appearance of bubbstons is analyzed semiquantitatively as a phase transition in an open system. The electrical and kinetic properties of these entities are studied. An electrolytic solution with suspended bubbstons—a disperse medium—is shown to be unstable with respect to a coagulation resulting in the formation of clusters. The ideas developed in this paper are used to interpret certain effects in acoustic and optical cavitation and also in the process by which gas bubbles form in the initial stage of the heating of a liquid (far from boiling).

1. INTRODUCTION

A long-standing problem in cavitation research is finding an explanation for the presence of stable microscopic gas bubbles in a pure liquid, free of any microscopic solid inclusions. In a sufficiently high concentration, these bubbles nucleate cavitation. That such formations must be present follows from the numerous classic studies of cavitation which have shown that the rupture strength of real liquids (i.e., that negative pressure p^* which causes cavitation) is always substantially lower (by at least an order of magnitude) than the molecular strength, $p^* \sim \alpha n^{1/3} \sim 10^4$ atm (α is the surface tension, and n is the density of the liquid particles), even if the liquids are thoroughly purified beforehand. The only possible reason for this lowering of the threshold would be the existence of stable gas bubbles in the liquid. Although this idea has become generally accepted, it does not yet have a solid theoretical foundation.

Two basic questions remain unanswered: (a) How can these bubbles of free gas form in a continuous medium (a liquid) containing a dissolved gas (e.g., air in water)?[1)] (b) If such a bubble has appeared, how can it remain stable?

The first question naturally arises if the liquid is not in a superheated state and is not subjected to a negative pressure $p \sim p^*$. In the opposite case, vapor bubbles may appear spontaneously in the liquid, as the result of thermal motion, and may act as nucleating centers of a new phase, which may in turn serve as nucleating centers for cavitation[1] or for laser breakdown. Far from the boiling point of the liquid, however, the probability for the formation of vapor nucleating regions is exceedingly low, so the question remains open.

The second question was first raised theoretically by Epstein and Plesset,[2] who showed that a free-gas bubble which appears in an equilibrium liquid-gas solution cannot be stable: It will always dissolve, since a solution which is at equilibrium (with respect to the external pressure) is supersaturated with respect to the gas pressure inside the bubble, $p_1 = p + 2\alpha/R$ (p is the external pressure, which is close to the hydrostatic pressure, and R is the bubble radius).[2)]

The possible presence of surface-active agents in real liquids (primarily, water) does not eliminate the question of the stability of the bubbles (as many authors have attempted to do qualitatively), since an admixture of a surface-active agent can only reduce the value of α. In other words, it can only reduce the rate at which the bubble dissolves; it cannot prevent the complete disappearance of the bubble. Experiments carried out back in the early part of this century (see Ref. 3 and the bibliography there) showed that there are electric charges at the surface of water (in particular, on the surface of an air bubble). Their origin was explained qualitatively in Ref. 4 as resulting from a selective adsorption of ions from the water onto the bubble surface. However, this idea of selective adsorption has not been pursued to the extent necessary. In a study of the ion theory of bubble stabilization, Akulichev[3] used only the very fact that there may be an electric charge Q on the surface of a bubble. An expression was derived for the stable radius by requiring a balance between the surface-tension pressure $2\alpha/R$ and the negative electrostatic pressure $2\pi\sigma^2/\varepsilon = Q^2/8\pi\varepsilon R^4$ ($\sigma = Q/4\pi R^2$ is the surface charge density, and ε is the dielectric constant of the liquid). That expression is

$$R_0 = \frac{Q^{2/3}}{(16\pi\alpha\varepsilon)^{1/3}} = \frac{\alpha\varepsilon}{\pi\sigma^2}. \tag{1}$$

The magnitude of the charge Q was not determined in Ref. 3, so the stabilization problem went unresolved.

In the present paper we are concerned primarily with a quantitative development of the idea of selective adsorption of ions on the surface of a bubble. This further study makes it possible to relate the charge Q and thus, according to (1), the radius of a stable bubble, R_0, to the properties of a solution consisting of a liquid, a gas, and a small impurity of an electrolyte. It follows from the results found below that stable microscopic bubbles with radii $R_0 \sim 10$–100 Å can exist in a liquid-gas solution if an "ionogenic" surface-active agent (i.e., one which dissociates into ions) with a sufficiently high adsorption energy is present, even if in only trace amounts (in a concentration $\lesssim 0.1$ *ppm*). A stable microscopic bubble consists of the gas bubble itself (the "core") and a spherical sheath of ions which cancels the charge of the bubble, Q. This stable core-plus-sheath formation might be thought of as an independent particle, which we will call a "bubbston" (from the English "bubble stabilized by ions").

We will also examine the question of the spontaneous appearance of bubbstons. Here we mean a nonequilibrium phase transition in an open system: the appearance of a dissipative structure in the form of a spherical cavity in a continuous medium. We conclude the paper with a discussion of certain mechanical and electrical properties of bubbstons.

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This discussion leads to an interpretation of many experimental facts.

To conclude this Introduction, we note that we will be drawing on such concepts as a hydrophobic or hydrophilic nature of ions and a negative and positive hydrotaxis, respectively. Although these concepts and their physical meaning were introduced in connection with aqueous electrolytic solutions (Ref. 5, for example), they are general in nature. The results derived below can be regarded as valid for a broad range of liquid solvents. In speaking in terms of an aqueous electrolytic solution, we are implying no more than that two types of ions can exist simultaneously in the solution: hydrophobic ions, with an adsorption energy which is high (in comparison with kT), and hydrophilic ions, with a low adsorption energy.

2. STABILIZATION OF FREE-GAS BUBBLES IN DILUTE ELECTROLYTIC SOLUTIONS

Let us consider a gas bubble in a dilute aqueous electrolytic solution, which we assume to be binary, symmetric, and singly charged. We assume that the electrolyte concentrate is quite low (we will be more specific regarding the restriction on the average ion density n_0 in the discussion below). The solution is at a temperature T and under an external pressure p. It has the equilibrium concentration (corresponding to the given T and p) of dissolved gas. We furthermore assume that the ions of one type (for definiteness, the positive ions) have hydrophobic properties and are thus surface-active, with an adsorption energy U at the bubble surface which is quite large in comparison with kT. In contrast, we assume that the ions of the other type have hydrophilic properties (and, correspondingly, $U \ll kT$).

In polar liquids with a large value of ε (e.g., water), an ionogenic nature of a surface-active agent is more the rule than the exception. Because of their surface-active properties, positive ions adsorb on the surface of a bubble. As a result, a positive electric charge forms on the bubble, with some charge density σ. The state of the bubble is generally unstable, and its radius R and charge density σ vary in time. Corresponding to a stable state are both a mechanical equilibrium and a diffusion equilibrium of the bubble with the solution. At mechanical equilibrium, the gas pressure inside the bubble, p_1, is equal to the pressure at the bubble surface: $p_1 = p + 2\alpha/R - 2\pi\sigma^2/\varepsilon$ (we are assuming that the hydrostatic pressure is equal to the external pressure). The time scale of the relaxation to this equilibrium is $\tau_M \sim R/(p_1/\rho)^{1/2}$ (this is the Rayleigh formula; ρ is the density of the liquid). In mechanical equilibrium, however, the gas density inside the bubble and also the surface density of adsorbed ions are generally not in equilibrium with, respectively, the volume densities of gas and positive ions dissolved in the liquid, and we have $2\alpha/R \neq 2\pi\sigma^2/\varepsilon$. This equilibrium is reached thanks to diffusion of gas molecules across the surface of the bubble and diffusion of ions to the surface of the bubble. The time scale of the first of these processes is R^2/D, and that of the second is R^2/D_E, where D is the diffusion coefficient of the gas molecules, and D_E is an effective diffusion coefficient of the ions. The latter diffusion coefficient incorporates the retardation of the process due to the Coulomb repulsion of ions from the bubble surface [see (5)]. The time scale for reaching diffusive equilibrium is

$$\tau_d \sim R^2/D_E \sim \tau_M (R/D_E)(p_1/\rho)^{1/2} \gg \tau_M,$$

since the condition $R \gg D_E/(p_1/\rho)^{1/2}$ always holds [since we have $D_E < D \sim 10^{-5}$ cm^2/s, and $(p_1/\rho)^{1/2} \sim 10^3$ cm/s]. We can therefore assume that diffusive relaxation processes are always occurring in mechanical equilibrium.

In the stable state of the bubble, the equality $2\alpha/R = 2\pi\sigma^2/\varepsilon$ is satisfied, and the diffusion flux of positive ions toward the bubble (the adsorption flux) becomes balanced by the desorption flux. The flux density of the desorption of ions is[7]

$$j_D = \gamma \nu_0 \exp(-U/kT), \tag{2}$$

where $\gamma = \sigma/\varepsilon$ is the surface density of adsorbed ions, and $\nu_0 = 1/\tau_0$ is the frequency at which an adsorbed ion oscillates around its temporary equilibrium position.

The adsorption flux density is

$$j_{AD} = D_i \left(\frac{dn}{dr}\right)_{r=R}, \tag{3}$$

where $n = n(r)$ is the density of positive ions at a distance r from the center of the bubble, and D_i is the diffusion coefficient for these ions. For solutions which are sufficiently dilute (more on this below), this diffusion coefficient is approximately the same as the diffusion coefficient for neutral particles, D. On the basis of the Boltzmann law, we can write the ion density as $n(r) = n_0 \exp(-e\varphi/kT)$, where $\varphi = \varphi(r)$ is the electric potential which is set up in the solution around the positively charged bubble. This picture [for $n(r)$] is of course valid only for sufficiently dilute solutions, for which the average energy of the Coulomb interaction of an ion with its nearest neighbor $[e^2 n^{1/3}(r)/\varepsilon]$ is small in comparison with the energy of the interaction of this ion with the electric field $e\varphi(r)$. Since this condition should be satisfied for ions with charges of both signs, it can be written

$$n_0 \ll (\varepsilon\varphi/e)^3 \exp(-|e\varphi|/kT). \tag{4}$$

As we will see below, for the problem at hand, this condition on n_0 is more restrictive than the usual condition that the "gas of ions" be ideal, $n_0 \ll (\varepsilon kT/e^2)^3$.

Determining the potential $\varphi(r)$ is the classic Debye–Hückel problem[7,8] (see Sec. 4 for more details). However, we do not need to solve this problem in order to calculate $(dn/dr)_{r=R}$ under condition (4), since we need to know the distribution $\varphi(r)$ only near the surface of the bubble, where this distribution is $4\pi R^2\sigma/\varepsilon r$. As a result, we find the following expression for the adsorption flux density from (3):

$$j_{AD} = D_E \frac{n_0}{R}, \qquad D_E = D_i \frac{4\pi R\gamma e^2}{\varepsilon kT} \exp\left(-\frac{4\pi R\gamma e^2}{\varepsilon kT}\right). \tag{5}$$

On the basis of (2) and (5), the equality $j_{AD} = j_D$ establishes a relationship between the stable value R_0 of the radius and the stable value of the surface density, γ_0:

$$\gamma_0 = \frac{\varepsilon U}{4\pi e^2 R_0} F(T, n_0, U), \tag{6}$$

where

$$F = 1 - \frac{kT}{U} \ln \frac{\varepsilon kT}{4\pi D e^2 n_0 \tau_0}. \tag{7}$$

A simultaneous solution of Eq. (6) and the equation $2\alpha/R_0 = 2\pi e^2\gamma_0^2/\varepsilon$ yields the relationships between the stable values R_0 and γ_0, on the one hand, and the parameters of the medium, on the other:

$$R_0=\frac{\varepsilon U^2}{16\pi\alpha e^2}F^2, \tag{8}$$

$$\gamma_0=\frac{4\alpha}{UF}. \tag{9}$$

In the stable state, the total number of adsorbed ions is

$$N_{i0}=4\pi R_0^2\gamma_0=\frac{\varepsilon^2U^3}{16\pi\alpha e^4}F^3.$$

In using these expressions one should bear in mind that the coefficient α generally depends on the density γ, with $d\alpha/d\gamma<0$ (Refs. 6 and 8). As we know, even a small admixture of a surface-active agent can lower the value of α by a factor of 2 or 3.

It can be seen from (6)–(9) that a stabilization is possible only if the adsorption energy is sufficiently high; i.e., there is a threshold in U. The threshold value, U_0, is found from the condition $R_0=R_{0\min}$, where $R_{0\min}$ is the minimum radius at which a bubble could be stable. This minimum radius is naturally found from the equation $N_{\min}=(4\pi R_{0\min}^3/3)p/kT$, where $N_{\min}$ is the smallest number of gas molecules which a stable bubble must contain. As we will see below, this threshold is an extremely weak function of the specific value of $N_{\min}$ (it varies as $N_{\min}^{1/6}$), so we can set $N_{\min}\sim 1$ in numerical estimates. From (7) and (8), we find the following expression for the threshold absorption energy U_0:

$$U_0=AkT+\Delta, \tag{10}$$

where

$$A=\ln\frac{\varepsilon kT}{4\pi De^2n_0\tau_0},\qquad \Delta=5\left(N_{min}\frac{kT}{p}\right)^{1/6}\left(\frac{\alpha e^2}{\varepsilon}\right)^{1/2}. \tag{11}$$

It follows from the condition $U>U_0$ and from (6) and (10) that

$$1>F>\frac{1}{1+AkT/\Delta}. \tag{12}$$

We turn now to condition (4), which imposes a limit on the ion density. From (6) and (7) we have

$$\frac{\varepsilon\varphi(R_0)}{e}=4\pi R_0\gamma_0=\frac{\varepsilon UF}{e^2}<\frac{\varepsilon U}{e^2},$$

$$\frac{e\varphi(R_0)}{kT}=\frac{4\pi R_0\gamma_0e^2}{\varepsilon kT}=\frac{UF}{kT}>\frac{\Delta}{kT}.$$

Substituting this result into (4), we find the condition

$$n_0\ll\left(\frac{\varepsilon UF}{e^2}\right)^3\exp\left(-\frac{UF}{kT}\right). \tag{13}$$

Note that this condition on n_0 is the condition under which our quantitative results in (6)–(9) are valid; it is not the condition for the occurrence of the gas-bubble stabilization itself.

Let us look at some estimates for an aqueous solution. The quantities A and Δ are extremely weak functions of the properties of the medium. For example, a change in the concentration of the electrolyte, n_0, by an order of magnitude changes U_0 by $2.3kT$, which is about 60 meV $\simeq$ 1.4 kcal/mole at room temperature. Over the entire temperature interval 273 K $<T<$ 373 K, for an electrolyte concentration of 0.03 *ppm* ($n_0=10^{15}$ cm^{-3}), for $p=1$ atm, for $D=10^{-5}$ cm^2/s, for $\tau_0=10^{-12}$ s, and for $\alpha=25$ erg/cm^2, we have (highly accurately) $\Delta=0.45$ eV $=10.3$ kcal/mole and $A=18.4$. At $T=273$ K the threshold energy is $U_0=0.88$ eV $=20$ kcal/mole; at $T=373$ K it is $U_0=1.04$ eV $=24$ kcal/mole.

With $U=1$ eV $=23$ kcal/mole and $T=300$ K, we find the radius $R_0=20$ Å and the density $\gamma_0\simeq 10^{14}$ cm$^{-2}\ll n_1^{2/3}\sim 10^{15}$ cm^{-2} (n_1 is the density of water particles). The total number of adsorbed ions is $N_{i0}\approx 50$. It is easy to verify that condition (13) holds in this case (the right side is $\sim 10^{16}$ cm^{-3}).

With $R_0=20$ Å and at a pressure $p=1$ atm, there is, on the average, only one molecule of dissolved gas inside a stable bubble $[N=(4\pi/3)R_0^3p/kT\approx 1)]$. Such a bubble is a sort of trap for single molecules. As the molecule collides with the bubble wall, at a frequency $v_T/2R_0$, it transfers a momentum $2m_1v_T[(v_T/2R_0)/4\pi R_0^2]=kT/(4\pi R_0^3/3)$, equal to the external pressure p to a unit area of the bubble wall per unit time (v_T is the average thermal velocity of the molecule, and m_1 is its mass). In our estimates, the value $R_0=20$ Å was found at an ion density $n_0\sim 10^{15}$ cm^{-3}. With increasing density n_0 (under otherwise equal conditions), the stable radius R_0 should increase. In the process, however, condition (13)—the condition under which our quantitative results are valid—may be violated (again, this is not the condition for the stabilization effect itself).

If the adsorption energy U is given, we can speak of a critical temperature T_c: For $T<T_c$, stable gas bubbles exist in the solution, while for $T>T_c$ they do not. The temperature $T_c=T_c(U,n_0,p)$ is found from the following equation, according to (10):

$$kT_c=\frac{U-\Delta}{A(T_c)}, \tag{14}$$

where

$$A(T_c)=\ln\left(\varepsilon kT_c/4\pi Dn_0e^2\tau_0\right).$$

The analysis above was based on the assumption that the medium initially contains a gas bubble in mechanical equilibrium. We turn now to the problem in which a bubble appears spontaneously in a liquid electrolytic solution.

3. SPONTANEOUS APPEARANCE OF FREE-GAS BUBBLES

The problem which we take up here is the problem of a nonequilibrium phase transition accompanied by the formation of structure: a gas bubble in a continuous medium. Like other problems of self-organization in open systems, this problem is very difficult to deal with on a rigorous quantitative level. The results below should be regarded as merely estimates, which (we believe) support the validity of the qualitative physical arguments on which our solution of the problem is based. A fundamental idea here is that the spontaneous appearance of a cavity—a gas bubble—in an electrolytic solution is a process which includes a stage in which a droplet of ion condensate forms in the solution. After this droplet reaches a certain size, it becomes unstable: It begins to "evaporate," and the volume of solution which it occupies becomes filled with the dissolved gas.

We consider a positive (hydrophobic) ion surrounded by water molecules (water is the solvent). The hydrophobic properties of an ion not only determine its ability to undergo adsorption on a water surface but also give rise to so-called negative hydrotaxis.[5] This hydrotaxis is seen in the circumstance that the potential barrier between water molecules becomes lower in the immediate vicinity of the ion, and these ions become more mobile. Their density near the ion turns out to be lower than the density in pure water. More rigorously, we could say that the distance from the ion to the first peak on the radial profile of the water molecules is greater than the corresponding distance in the case of pure water. This difference should in turn lead to the existence, near the positive ion, of a potential well for a negative ion having hydrophilic properties (and positive hydrotaxis).

The random diffusion of such an ion near the positive ion should give rise to a stable neutral ion dimer in the solution. The same arguments lead to the conclusion that the subsequent diffusion of ions to this dimer should cause the latter to grow i.e., condensation of ions accompanied by the formation of a neutral droplet. The reason why this droplet is neutral is that each negative ion occupies a position on the surface of the droplet in the potential well formed by a positive ion which has already condensed. The heat of condensation released in the process is dissipated in the surrounding liquid. Since the average energy of the Coulomb interaction of the ions in the droplet is zero, energy does not accumulate in the droplet.

These arguments remain valid as long as the dimensions of the droplet are sufficiently small, and an interface has not yet formed between the solution and the droplet. Denoting by R_{dr} the radius of the droplet, we see that the formation of an interface corresponds to the condition $R_{dr} \gg n_{dr}^{-1/3}$, where n_{dr} is the density of ions in the droplet (we are assuming that the volumes per ion for the ions of the different types are comparable in magnitude). The droplet becomes unstable: Positive ions of the droplet begin to adsorb on the interface. As a result, the negative change inside the droplet is no longer canceled, and the Coulomb field which arises in the droplet repels the negative ions beyond the interface: The droplet begins to "evaporate." The evaporation rate is limited by the diffusion of the positive ions of the droplet to the surface, with a time scale R_{dr}^2/D. However, the region which has been freed of ions should be filled with dissolved gas over the same time scale. This process—the evaporation of the droplet accompanied by a simultaneous filling of the cavity with gas—should cause a gas-bubble structure to appear, a nucleating region in mechanical equilibrium. The radius of the nucleating region which has arisen, R_n, should be determined by minimizing the thermodynamic potential

$$W(R)=4\pi R^2\alpha+p\frac{4\pi R^3}{3}+\frac{(eN)^2}{2\varepsilon R}. \tag{15}$$

The first term of this sum is the surface energy of the nucleating region, the second is the energy of the gas in this nucleating region, and the third is the energy of the electric field of the nucleating region, which carries a charge eN, where $N=(4\pi/6)n_{dr}\cdot R_{dr}^3$ is the number of positive ions in the droplet. From the equation $dW/dR=0$ we find

$$R_n=\left(\frac{\pi e^2 n_{dr}^2}{36\alpha\varepsilon}\right)^{1/3} R_{dr}^2 \tag{16}$$

[here we have used $p \ll 2\alpha/R_n$; see (17)]. Since the rate at which the droplet evaporates and the rate at which it becomes filled with gas are on the same order of magnitude, we can assume $R_n \simeq R_{dr}$. Substituting this approximation into (16), we find a final expression for the radius of the nucleating region:

$$R_n \approx \left(\frac{36\alpha\varepsilon}{\pi e^2 n_{dr}^2}\right)^{1/3} \tag{17}$$

[here $2\alpha/pR_n \sim (\alpha^2 e^2 n_{dr}^2/\varepsilon p^3)^{1/3} \gg 1$]. The number of positive ions which accumulate in the droplet before it decays (before evaporation begins) is given by

$$N_i=\frac{4\pi}{6}n_{dr}R_n^3 \approx \frac{24\alpha\varepsilon}{e^2 n_{dr}}. \tag{18}$$

With $n_{dr} \simeq 3\cdot 10^{21}$ cm^{-3}, for water, we thus find $R_n \simeq 30$ Å and $N_i \simeq 140$ ions.

The radius of a nucleating region, R_n, does not depend explicitly on either the temperature or the density of the electrolyte. The rate at which nucleating regions form (i.e., the number of these regions which appear per unit time per unit volume), on the other hand, should depend on these parameters. Determining this rate is a kinetic problem, which we will not go into. If, at a given temperature T and a given electrolyte density n_0, the radius R_n of a bubble which has appeared spontaneously is greater than (or, on the contrary, less than) the stable radius $R_0(T,n_0)$, the balance between the process of adsorption and desorption of positive ions will be disrupted. As a result, the bubble will reach diffusive equilibrium, and its radius will become equal to $R_0(T,n_0)$. In other words, the bubble will become stable. In this manner, a bubbston forms.

4. CERTAIN PROPERTIES OF BUBBSTONS

a) Electrical properties. A bubbston consists of a stable gas microbubble (a core) which carries a charge $Q_0=4\pi R_0^2\gamma_0 e$ on its surface and which is surrounded by a spherical sheath of ions with a charge density $\rho(r)$, which has a canceling charge Q_0. As a result, the bubbston as a whole is neutral:

$$Q_0+4\pi\int_{R_0}^{\infty}\rho(r)r^2\,dr=0. \tag{19}$$

We will say that a bubbston is positive (negative) if the charge Q_0 is greater than (less than) zero. Outside the core there is a spherically symmetric electric field. Denoting the potential of this field by $\varphi(r)$, we can write the charge distribution in the sheath as

$$\rho(r)=-en_0[\exp(e\varphi/kT)-\exp(-e\varphi/kT)],\quad r \geqslant R_0. \tag{20}$$

The potential $\varphi(r)$ itself must satisfy the Poisson equation

$$\nabla^2\varphi=-\frac{4\pi}{\varepsilon}\rho(r)=\frac{4\pi}{\varepsilon}en_0[\exp(e\varphi/kT)-\exp(-e\varphi/kT)]. \tag{21}$$

With a given value at $r=R_0$ it must vanish at infinity. The validity of representation (20) and thus of Eq. (21) is obviously restricted by conditions (4) and (13); i.e., the solution must be sufficiently dilute.

Equation (21) can be solved easily under the condition $e\varphi/kT \ll 1$ [or, more rigorously, under the condition

$(1/6)(e\varphi/kT)^2 \ll 1]$. This solution was first carried out by Debye and Hückel.[7,8] In this case we have $\rho(r) = -2n_0e^2\varphi/kT = -(\varepsilon/4\pi)\varphi(r)/a^2$, where

$$a=\left(\frac{\varepsilon kT}{8\pi e^2 n_0}\right)^{1/2}, \tag{22}$$

and the solution of Eq. (21) is[7]

$$\varphi(r) = \frac{Q_0}{\varepsilon(1+R_0/a)r}\exp\left(-\frac{r-R_0}{a}\right), \quad r \geqslant R_0. \tag{23}$$

It is easy to verify that neutrality condition (19) is satisfied for this solution. The Debye radius a determines the thickness of the ion sheath. For an aqueous solution with $n_0 \sim 10^{15}$ cm^{-3} this radius would be $a \sim 3\cdot 10^{-5}$ cm, so we would have $(R_0/a) \sim 10^{-2}$.

The solution (23) does not, on the other hand, describe the potential of the bubbston for $r \geqslant R_0$. Specifically, we see from (23) that we have $\varphi_{\max} = \varphi(R_0) = 4\pi R_0\gamma_0 e/\varepsilon$ and $e\varphi_{\max}/kT = UF/kT > \Delta/kT$ [here we have used Eqs. (6), (10), and (21)]. Since we have $\Delta/kT > 1$, the ratio $e\varphi/kT$ near the core of the bubbston is always greater than unity, so the actual potential distribution in this region should differ from (23). It is easy to show that for highly dilute solutions, for which the ratio R_0/a is small, a Debye–Hückel solution of the form (23) always describes the peripheral part of the bubbston potential $\varphi(r)$. With decreasing value of the ratio R_0/a, the total thickness of the ion sheath tends toward the Debye radius a. Actually, there is generally a third length scale in this problem (in addition to R_0 and a), $a_1 > R_0$. This third length scale is such that the total charge Q_1 of the core and of the adjacent layer of the ion sheath, $R_0 \leqslant r \leqslant a_1$, i.e., the charge

$$Q_1 = Q_0 + 4\pi\int_{R_0}^{a_1}\rho(r)r^2\,dr \tag{24}$$

is so small that the potential distribution at $r > a_1$ satisfies the condition $e\varphi/kT \ll 1$. It must therefore be of the form

$$\varphi(r) = \frac{Q_1}{\varepsilon(1+a_1/a)r}\exp\left(-\frac{r-a_1}{a}\right), \quad r \geqslant a_1. \tag{25}$$

The relationship between a_1 and Q_1 can be established from the condition $e\varphi(a_1)/kT = 1$, i.e., from the equation

$$\frac{a_1}{a}\left(1+\frac{a_1}{a}\right) = \frac{eQ_1}{\varepsilon kTa}. \tag{26}$$

Since $Q_1 < Q_0$, the right side of this equation is smaller than $4\pi R_0\gamma_0 e^2/\varepsilon kTa = (UF/kT)(R_0/a)$. We thus find that at $(R_0/a) \ll (kT/UF)(\sim 1/30)$ the right side of (26) is less than one, so we have $a_1/a \sim eQ_1/\varepsilon kTa \ll 1$. Substituting $a_1 = eQ_1/\varepsilon kT$ into the right side of (24), we find an equation which relates Q_1 and Q_0. Once we know this relationship, we have completely determined the bubbston potential profile at $r \geqslant a_1$.

There is the interesting question of the interaction of bubbstons with each other and with the wall of the vessel. Let us consider two bubbstons, one at the point $\mathbf{r} = 0$ (this will be the "first" bubbston), and one at $\mathbf{r} = \mathbf{l}$. The volume density of the ponderomotive forces exerted on the sheath of the second bubbston by the first bubbston is

$$\mathbf{f} = -\frac{d\varphi(r)}{dr}\rho(r_1)\frac{\mathbf{r}}{r},$$

where $r_1 = (l^2 + r^2 - 2rl\cos\theta_1)^{1/2}$, and θ_1 is the angle between $\mathbf{r}$ and $\mathbf{l}$. Imposing the assumption $l \gtrsim 2a$, so that the sheaths of the bubbstons do not overlap substantially, we can assume that $\varphi(r)$ and $\rho(r_1)$ refer to the peripheral parts of the sheaths. We can thus write $\rho(r_1) = -(\varepsilon/4\pi)\varphi(r_1)/a^2$, and we can find $\varphi(r)$ from expression (25). As a result, we find the following expression $\mathbf{f}$ for the force $(a_1/a \ll 1)$:

$$\mathbf{f} = -\frac{Q_1^2(1+r/a)}{4\pi\varepsilon a^2r^2r_1}\exp\left(-\frac{r+r_1-a_1}{a}\right)\frac{\mathbf{r}}{r}. \tag{27}$$

This force is directed toward the center of the first bubbston; i.e., the first bubbston attracts the second.

The problem of the interaction of a bubbston with a wall can be solved by the well-known image method from electrostatics.[9] It is easy to show that the interaction of a positive bubbston with a metal wall at a distance h is equivalent to the interaction of the same bubbston with a negative bubbston at a distance $2h$. In other words, the bubbston should be repelled from such a wall. If the wall is an insulator and has a dielectric constant $\varepsilon' \ll \varepsilon$, the interaction with the wall is equivalent to an interaction with a bubbston of the same sign (at twice the distance). In other words, the bubbston is attracted toward such a wall.

The conclusions which we have reached regarding the directions of the interaction forces hold for distances l and h such that there are no perturbations of the bubbston sheaths. As these distances decrease, and the sheaths become perturbed, the interaction should always reduce to a repulsion, according to the Le Chatelier–Brown principle.

Let us also take a brief look at the effect of static external electric fields on a bubbston. A bubbston should remain stable in the face of such external agents as long as the field of the bubbston core, $E_0 = 4\pi\gamma_0 e/\varepsilon$, is strong in comparison with the external field E. For an aqueous solution with $\gamma_0 \sim 10^{14}$ cm^{-2}, the core field is $E_0 = 4\pi\gamma_0 e/\varepsilon \gtrsim 2\cdot 10^6$ V/cm. If $E \ll E_0$, a bubbston may—while remaining stable overall—lose its electrical neutrality as the result of the "detachment" of some outer (peripheral) ions of the sheath. We can thus speak in terms of an "ionization" of the bubbston. A ponderomotive force ZeE (Z is the charge state) should be exerted by the external field on an "ionized" bubbston. This force should in turn give rise to an electrophoresis.

b) Kinetic properties. During the mechanical motion of a bubbston, its ion sheath should in general be perturbed by viscous forces. A factor acting to stabilize the structure of the sheath is the electrostrictive pressure $p_{\rm str}(r)$, which results from the presence of an electric field[10] $E_0(r) = -d\varphi/dr$ in the sheath. This pressure is $p_{\rm str} = YE_0^2(r)$, $Y = (1/8\pi)(\rho\partial\varepsilon/\partial\rho)$. If the bubbston velocities are sufficiently low, the perturbation of the sheath is negligible. The necessary condition here is that the gradient of the viscous stress be small in comparison with the gradient of the electrostrictive pressure. As was shown above, the sheath thickness is always determined by the Debye radius a in sufficient dilute solutions, so the condition under which a bubbston will retain its structure as it moves at a velocity u can be written $\eta u/a^2 \ll p_{\rm str}/a$ or

$$u \ll \frac{YaE_0^2}{\eta}, \tag{28}$$

where η is the viscosity of the solution. Assuming $E_0 \sim E_0(R_0) = 4\pi\gamma_0 e/\varepsilon$ for an aqueous solution, we find the condition $u \ll 10^3$ cm/s. We will assume below that this condition holds, and we will treat the motion of the bubbston as the motion of a liquid droplet of radius a (which has the same viscosity as the solution itself). The condition on the velocity u which we have found means that the Reynolds number $\mathrm{Re} = \rho u a/\eta$ is small (ρ is the density of the solution).

Also acting on the bubbston are the buoyant force $F_A = (4\pi/3)R_0^3\rho g$ (g is the acceleration due to gravity) and the gravitational force $F_g = 4\pi R_0^2\gamma_0 g M/N_A$ (M is the molecular weight of the positive ions, and N_A is Avogadro's number). The total force is thus

$$F = \frac{4\pi R_0^3\rho g}{3}\left(1 - \frac{3M\gamma_0}{R_0\rho N_A}\right). \tag{29}$$

With $R_0 \simeq 20$ Å, $\gamma_0 \simeq 10^{14}$ cm^{-2}, and $\rho \approx 1$ g/cm^3, we find the ratio $3M\gamma_0/R_0\rho N_A \approx M/400$. In other words, for $M < 400$, the bubbstons should float up to the surface of the vessel. The velocity at which they do so, u_0, can be determined by setting the Stokes friction force $F_{\mathrm{fric}} = 5\pi\rho\nu a u_0$ (see Ref. 11) equal to the force F. This velocity is found to be

$$u_0 = BF = \frac{4}{15}\frac{R_0^2}{\nu}\frac{R_0}{a} g\left[1 - \frac{3M\gamma_0}{R_0\rho N_A}\right], \tag{30}$$

where $B = 1/5\pi\eta a$ is the mobility of the bubbstons, and $\nu = \eta/\rho$ is the kinematic viscosity of the solution. For an aqueous solution with $R_0 \approx 20$ Å this velocity turns out to be $u_0 \sim 10^{-11}$ cm/s (here we have set $R_0/a \sim 10^{-2}$). Actually, however, bubbstons may float up much more rapidly. The reason is that a disperse medium—in our case, the electrolytic solution with suspended bubbstons—is unstable against a coagulation effect, i.e., coalescence of bubbstons resulting in the construction of larger formations: bubbston clusters. The possible existence of such clusters was first pointed out in a study[11] of optical cavitation. Since bubbstons attract each other, each event in which bubbstons come close to each other should be effective; i.e., the coagulation should be "fast" coagulation.[12]

Let us estimate the equilibrium density n_b of bubbstons with radii R_0 (i.e., the number of bubbstons per unit volume of the solution). Denoting by n_s the density of dissolved gas molecules in the saturation state, and denoting by δ the relative amount of free gas in the overall gas content of the liquid, we have $\delta n_s = (p/kT)(4\pi/3)R_0 n_b$. From Henry's law we have $n_s = K(T)p/kT$, where $K(T)$ is the Henry coefficient. For n_b we then find

$$n_b = \delta K\left(\frac{4\pi}{3}R_0^3\right)^{-1}. \tag{31}$$

For air in an aqueous solution under normal conditions we would have $K = 0.02$; with $R_0 \simeq 20$ Å, we would find $n_b = 6\cdot 10^{17}\cdot\delta$ (cm^{-3}). A wide range of values has been reported for the coefficient δ in the literature: from 10^{-10} to 10^{-2} (Ref. 13). We can shrink this range substantially by making use of the obvious condition $n_b \ll (1/2a)^3$. For an aqueous solution with an electrolyte density $n_0 \sim 10^{15}$ cm^{-3}, we would thus have $n_b \ll 3\cdot 10^{12}$ cm^{-3}. In the estimates below, we assume $\delta \sim 10^{-7}$ and $n_b \sim 10^{11}$ cm^{-3}.

Let us calculate the coagulation time θ for bubbstons having an initial density n_b, for a process resulting in the formation of clusters of N_b individual bubbstons. In a unit volume of the medium we single out $m \ll n_b$ arbitrary bubbstons, and we examine the kinetics of their growth as clusters, as the result of the coagulation of the other bubbstons on them. The diffusion flux density of bubbstons to the surface of a growing cluster is $j_d = (D_1/R)[(n_b - \beta m R^3/a^3)]$, where $R = R(t)$ is the instantaneous radius of the cluster, $D_1 = kTB = kT/5\pi\rho\nu a$ is the Brownian diffusion coefficient of the bubbstons, the quantity $\beta(R/a)^3$ determines the number of bubbstons in a cluster at a given instant, and the coefficient β (which is less than one) is determined by just how compactly the cluster of bubbstons is packed (in the hard-sphere model, for spheres of radius a, we would have $\beta = 0.74$ in the case of the closest packing). The rate of growth of the cluster volume, $(d/dt)(4\pi R^3/3)$ is equal to the total flux of bubbstons to the surface of the cluster, $j_d 4\pi R^2$, multiplied by the volume per bubbston, $4\pi a^3/3\beta$. As a result we find the equation

$$x\frac{dx}{dt} = 1 - x^3, \tag{32}$$

where

$$x = \left(\frac{\beta m}{n_b}\right)^{1/3}\frac{R}{a}, \quad t_1 = \left(\frac{4\pi}{15\beta^{1/3}}\right)\frac{t}{\theta}, \qquad \theta = \frac{\rho\nu}{kTn_b^{1/3}m^{2/3}}. \tag{33}$$

The initial condition in Eq. (32) is $x(0) = (\beta m/n_b)^{1/3} \ll 1$. At $t > 0$, the quantity x tends monotonically toward its maximum value $x_{\max} = (\beta m/n_b)^{1/3}R_{\max}/a = 1$. This value corresponds to a number $N_b = \beta(R_{\max}/a)^3 = n_b/m$ of bubbstons in a cluster at the point at which complete coagulation of all the remaining bubbstons has occurred on the m bubbstons which we have singled out. The time scale for the attainment of this complete coagulation is the time θ given by (33). This time can be written in the two equivalent ways $\theta = \theta_{1/2}(n_b)N_b^{2/3} = \theta_{1/2}(m)N_b^{-1/3}$, where N_b is to be understood as the maximum number of bubbstons in a cluster (i.e., $N_b = n_b/m$), and the time

$$\theta_{1/2}(n) = \frac{\rho\nu}{kTn} \tag{34}$$

is the coagulation time introduced by Smoluchowski, over which the initial density of disperse particles, n, decreases by half.[12] From these expressions we find $\theta \ll \theta_{1/2}(m)$; i.e., the further growth of clusters as a result of their coagulation with each other can be ignored.

The velocity u_0 with which a cluster of N_b bubbstons floats up can be determined by equating the Archimedes force $(4\pi R_0^3/3)\rho g N_b$ to the friction force $F_{\mathrm{fric}} = 5\xi\rho\nu R u_0$, where $R = a(N_b/\beta)^{1/3}$. The coefficient $\xi \gtrsim 1$ is the correction in the Stokes formula for the deviation of the surface of the cluster from an ideal sphere. We find

$$u_0 = \frac{4\beta^{1/3}R_0^2}{5\xi\nu}\frac{R_0}{a} g N_b^{2/3}. \tag{35}$$

A comparison of (35) with (30) shows that the velocity with which a cluster floats up is greater than the velocity of an individual bubbston by a factor of about $N_b^{2/3}$.

The bubbstons which are floating up carry gas dissolved in the liquid up to the surface of the liquid. As a result, there should be a vertical gradient of the total concentration of dissolved gas in the liquid. This gradient should be directed upward. The corresponding diffusive flux of gas should be directed downward. The steady-state (equilibrium) conditions are evidently reached when, in the course of the diffusion of gas to a depth h in the vessel, the only clusters which manage to form are those whose floating-up time is large in comparison with the diffusion time h^2/D (we are of course assuming here that the time scale for the spontaneous formation of the bubbstons themselves is short in comparison with all the other time scales of this problem). From the relation $h^2/D \sim (\rho\nu/kTn_b)N_b^{2/3}$ we thus find an expression (valid in order of magnitude) for the steady-state (equilibrium) number of bubbstons in a cluster, N_b^0:

$$N_b^0 \sim \left(\frac{kTn_bh^2}{D\rho\nu}\right)^{3/2}. \tag{36}$$

The time scale for the floating up of such bubbstons, h/u_0, is, according to (35),

$$\frac{h}{u_0} \sim \frac{15\xi}{4\beta^{1/3}}\frac{\rho D\nu^2}{R_0^2gkTn_bh}\frac{a}{R_0}, \tag{37}$$

and the ratio of this time to the diffusion time h^2/D is

$$\frac{(h/u_0)}{(h^2/D)} \sim \frac{15\xi}{4\beta^{1/3}}\frac{D^2\nu^2\rho(a/R_0)}{R_0^2gkTn_bh^3}. \tag{38}$$

With $h \sim 1$ cm, $R_0 \approx 20$ Å, and $R_0/a \sim 10^{-2}$, we find this ratio to be ~ 30 (i.e., the condition for a steady state is satisfied), and the time scale for the floating up of clusters is $\sim 3\cdot 10^6$ s ~ 1 month. The equilibrium number of bubbstons in a cluster, according to (36), $N_b \sim 10^7$, and the equilibrium cluster radius is $R_{0cl} = a(N_b^0/\beta)^{1/3} \sim 5\cdot 10^{-3}$ cm. The density of such clusters is $m \sim n_b/N_b^0 \sim 10^4$ cm^{-3}.

Clusters can of course also form at the walls of the vessel, which attract bubbstons. The number of bubbstons in such "wall" clusters may be substantially greater than N_b^0.

5. CONCLUSION

We believe that the results found here can serve as a starting point for reaching a more profound understanding of many physical phenomena which occur in liquids. We are referring primarily to such phenomena as cavitation and laser breakdown of liquids. The theory of acoustic cavitation has been developed in some detail (see, for example, the reviews[14,15]). That theory leads to results which agree qualitatively with experimental data (in terms of the thresholds for the onset of cavitation in water) only if one assumes that when the sound is first applied to the liquid the liquid already contains gas bubbles, nucleating regions with radii $R \gtrsim 3\cdot 10^{-5}$ cm. However, the time scale for such bubbles to float up to the surface is $h/u_0 \sim 10$ h. It is thus not possible to explain the presence of such bubbles in water which has been purified and left to stand for several days (these are the conditions to which the experimental data refer). It was suggested in Ref. 11 that the nucleating regions for cavitation are clusters which form from stable microscopic gas bubbles and that the cavitation cavity itself forms as the result of a rapid coalescence of these microscopic bubbles, stimulated by an external agent (sound or light).

The results derived above put this idea of a "cluster mechanism" for cavitation in a more concrete form. According to these results, the cavitation nucleating regions may be bubbston clusters which exist stably in liquid-gas solutions containing traces of ionogenic surface-active agents (a typical example of such a medium is distilled water). The application of sound to a cluster stimulates (in the negative-pressure phase) rapid coalescence of the cluster, resulting in the formation of a gas bubble with a radius $R_1 = R_0(N_b^0)^{1/3}$. For an aqueous solution under normal conditions, this radius would be $\approx 5\cdot 10^{-5}$ cm. The acoustic field itself thus creates the initial gas bubbles required for the development of cavitation cavities. In optical cavitation, for laser pulses in the nanosecond range, the leading mechanism appears to be a laser breakdown which occurs initially in individual bubbstons of a cluster. This process again leads to a rapid coalescence of the cluster. The bubbston-cluster mechanism also gives us a natural interpretation of the results of experiments in which the cavitation strength of distilled water has been observed to increase when the water was held in a static electric field for a long time.[15] The increase in strength is attributed to the removal of clusters from the region to which the field is applied, because of the electrophoresis of clusters caused by the ionization of bubbstons by the external electric field. Arguments regarding the bubbston-cluster structure of a liquid also provide a natural explanation for the picture of the appearance of gas bubbles floating upward in the initial stage of the heating of a liquid, in which the temperature of the liquid is far from the boiling point, and the probability for the formation of vapor bubbles is low. The widely accepted explanation for this effect, which is based entirely on the one fact that the solubility of gases in a liquid decreases as the temperature of the liquid rises (the Henry coefficient K decreases with T), is unsatisfactory, in our opinion. Our primary objection is that that explanation still requires the existence of stable microscopic bubbles as nucleating regions. These nucleating regions must be present if diffusion processes are to arise and to lead to a decrease in the concentration of dissolved gas. There are reasons to believe that a temperature increase may also stimulate a coalescence of clusters, resulting in the formation of the necessary nucleating regions. [The reason for this coalescence might be (first) an increase in the pressure inside individual bubbstons of a cluster or (second) a mutual perturbation of the ion sheaths of bubbstons, because of the increase in the Debye radius with increasing temperature; see (22).] This "thermal coalescence" should arise first at the walls of the vessel in which the liquid is heated, because these walls are at a higher temperature, and also because in the wall clusters the number N_b may be much greater than N_b^0. Correspondingly, of course, we observe the formation of gas bubbles in the initial stage of the heating of a liquid.

Finally, we repeat that the theory for the stabilization of gas bubbles derived above is valid only for dilute electrolytic solutions, in which the ion density n_0 satisfies condition (4) or (13) (for aqueous solutions under normal conditions we would have $n_0 \lesssim 10^{15}$ cm^{-3}). For many problems, this limitation is too restrictive. It would thus be very interesting to generalize this theory to the case of less dilute solutions.

[1] It is of course being assumed here that the liquid is in a steady state, and no source is introducing free gas into the liquid (there is no gas-bubble generator).

[2] If the initial radius of the bubble is sufficiently large, the bubble may float up to the surface of the liquid before it has had time to dissolve. This is what is usually observed when free gas bubbles are deliberately introduced into a liquid.

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