

Nature of sonoluminescence: Noble gas radiation excited by hot electrons in cold water

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(Received 8 October 1999)

It was proposed before that single bubble sonoluminescence (SBSL) may be caused by strong electric fields occurring in water near the surface of collapsing gas bubbles because of the flexoelectric effect involving polarization resulting from a gradient of pressure. Here we show that these fields can indeed provoke dynamic electric breakdown in a micron-size region near the bubble and consider the scenario of the SBSL. The scenario is (i) at the last stage of incomplete collapse of the bubble, the gradient of pressure in water near the bubble surface has such a value and a sign that the electric field arising from the flexoelectric effect exceeds the threshold field of the dynamic electrical breakdown of water and is directed to the bubble center; (ii) mobile electrons are generated because of thermal ionization of water molecules near the bubble surface; (iii) these electrons are accelerated in "cold" water by the strong electric fields; (iv) these hot electrons transfer noble gas atoms dissolved in water to high-energy excited states and optical transitions between these states produce SBSL UV flashes in the transparency window of water; (v) the breakdown can be repeated several times and the power and duration of the UV flash are determined by the multiplicity of the breakdowns. The SBSL spectrum is found to resemble a black-body spectrum where temperature is given by the effective temperature of the hot electrons. The pulse energy and some other characteristics of the SBSL are found to be in agreement with the experimental data when realistic estimates are made.

PACS number(s): 78.60.Mq

I. INTRODUCTION

Sonoluminescence refers to the phenomenon of light emission during acoustic radiation of a liquid and is associated with cavitation bubbles present in the liquid. The most controllable and promising experimental data were obtained for single bubble sonoluminescence (SBSL): picosecond UV radiation of a single bubble pulsating in the field of the sound wave [1,2].

Though the case of a single pulsating bubble is, of course, much simpler than cavitation in general, it turns out that the SBSL is a very complex phenomenon which still remains not completely understood. There is a vast literature devoted to SBSL that was recently reviewed in Ref. [2]. Interest in this phenomenon is stimulated, on the one hand, by the fact that in relatively simple and controllable experiments extraordinary conditions (ultrahigh pressures, temperatures, and ultrashort light flashes) are realized at the final stage of the bubble collapse; on the other hand, it looks promising to use the SBSL to construct a source of ultraviolet ultrashort flashes that is much cheaper than lasers.

The highly involved hydrodynamics of bubble collapse has been addressed in many papers that are reviewed in Ref. [2]. One of the most important problems to explain here is the very existence of stable pulsation of bubbles. Recently a theory has been developed [3,4] which explains this regime in terms of the dissolved gas diffusion and chemical reactions in the gas within the bubble. It has been shown that an accumulation of noble gas in the bubble takes place during pulsation of the bubble and that in a stable situation the gas in the bubble consists, almost entirely, of noble gas and, of course, of water vapor. These theoretical conclusions were

supported by the experimental data of Ref. [5].

Another key problem in SBSL is the mechanism of the light emission. Many mechanisms have been proposed, criticized, and reviewed to explain UV flashes radiated by the collapsing bubble [2]. The most popular of the suggested mechanisms are the adiabatic heating of the bubble gas [2,6,7], shock wave-Bremsstrahlung model [2,10–12], and the recently proposed proton-tunneling radiation as a result of a phase transition in water at ultrahigh pressure [13]. A general feature of these mechanisms is that extraordinary conditions are needed which can only be realized, if at all, at a very small bubble radius when the density of the bubble gas is close to the water density and both the hydrodynamics of the bubble and the properties of the bubble content and the neighboring liquid are not known from experiment but inferred from numerical simulations.

In this paper we show that the main characteristic features of SBSL can be explained without even making any assumption about the extraordinary conditions. We are far from saying that these extraordinary conditions are not present in experiments. What we mean is that there is another mechanism of the SBSL which occurs in water near the bubble surface but not in the bubble gas as has been assumed in the most popular models of SBSL [2]. Extraordinary conditions are not necessary for the operation of this mechanism even though it may well be the main cause of UV radiation. The mechanism under consideration is based on the idea put forward in Ref. [14] that SBSL occurs because of electric breakdown in strong electric fields arising near the bubble surface as a result of the flexoelectric effect, that is, the effect of polarization of water because of gradients of pressure [16]. Here we present a scenario and estimations that show

that within the hypothesis the main features of SBSL can be explained using relatively moderate parameters, e.g., temperatures $(5-10)\times 10^3$ K for the bubble gas [6], and the natural (expected) value of the flexoelectric coefficient of water [14].

Let us mention that Ref. [14] has left many questions to answer. The origin of the optical radiation of the bubble remains unexplained. The problem is that in the visible region pure water has very low levels of absorption and radiation due to interband optical transition [17]. Moreover the breakdown scenario is far from being clear. The mechanism of the breakdown in water (see, e.g., Ref. [18]) involves “lucky electrons” whose acceleration in the electric field leads to development of an avalanche. At ambient temperature the concentration of free electrons in water is quite negligible (the band gap is about 6.5 eV [17,18]) and it is impossible to find a “lucky electron” in a small volume near the bubble surface, i.e., in the region of high electric field, during the short time of the existence of this field. The spectacular synchronization of the emission pulses [2,19] that in the case of breakdown appears, at least at first sight, to be hardly compatible with the fact that we are dealing with a probabilistic situation. In addition, the reference to the Penning effect to explain the role of the noble gases is not convincing because the ionization energy of the metastable state is more than the band gap of water as distinct from the case of breakdown in gases where the Penning effect is pronounced.

In this paper we consider in more detail possible processes associated with the electric field arising from the flexoelectric effect near a bubble exhibiting SBSL. A common difficulty with theories of SBSL is that little is known about the parameters of gas in the bubble when the bubble radius is near its minimum value. Consensus exists about one point: it is far from being a gas, because the lowest limit of the radius is governed by the van der Waals repulsion and the minimum volume of the bubble is close to the van der Waals hardcore volume. The equations of state used for these conditions are not reliable at present. This is a challenging and fundamental problem but it is beyond the scope of this paper. What is now possible is to make order-of-magnitude estimations. That is why we shall first explain what values of relevant parameters are necessary for our scenario to be operative and then discuss whether our assumptions about these parameters are realistic. We include the value of the flexoelectric coefficient of water among these parameters as well. This coefficient has not been measured, unfortunately, and we use its estimated “natural” value but, from the other hand, the knowledge of its precise value would hardly be of decisive importance because the bubble gas parameters are not known precisely.

Let us describe shortly the proposed scenario. At certain short time interval, $\tau_c \sim 1$ ns, when the bubble radius is near its minimum, the acceleration of the radius and, therefore, the pressure gradient, assume gigantic values [2] and the sign of the pressure gradient is such as to create a strong (depolarizing) electric field directed to the center of the bubble in a thin water layer, ~ 1 μ m, near the bubble surface, because of the flexoelectric effect. What happens then is, in effect, screening of this depolarizing field by free electrons. Indeed, during the same time interval the temperature of the gas

sharply increases up to at least several thousand K, which owing to thermal excitation of the bubble gas and water in a thin layer near the bubble surface makes the concentration of free electrons appreciable. The free electrons are accelerated by the strong “flexoelectric” field up to energies sufficient to generate additional free electrons as a result of the electric breakdown of water. The hot electrons also collide with noble gas atoms dissolved in water and transfer them to higher energy excited states. Optical transitions from these states produce light radiation with a broad spectrum whose shape is determined mainly by the energy distribution of the hot electrons. The latter has the form of a Maxwell distribution with an effective electron temperature which can be very high. This is due to the fact that the noble gas atoms have a huge number of excited states with very high probabilities of optical transitions between them (see, e.g., Refs. [20,21]). Since the radiation occurs in the region of very strong and inhomogeneous electric fields the observed radiation spectrum is featureless. The characteristic time of the electric breakdown is much less than the characteristic time for the last stage of the collapse τ_c , i.e., the polarization can continue to change after the first breakdown and the electric field can reach the breakdown threshold value more than once. As a result, several breakdowns can take place during the time interval τ_c . During each breakdown the noble gas atoms are excited. An important specific feature of the noble gas atoms is the existence of long-living (metastable) excited states with a life time of up to several milliseconds (see, e.g., Refs. [20,21]). Therefore, once excited the noble gas atom can remain in the metastable state for the entire time interval $\tau_c \sim 1$ ns, and, possibly, for many periods of the acoustic wave (the period is about 30 μ s). That means that in the stationary state the longer is the pulse the more is its intensity.

The paper is organized as follows. In Sec. II we discuss the flexoelectric effect in water in more detail than in Ref. [14] and consider the sign of the flexoelectric field, which is crucial for the proposed scenario, at different stages of the bubble collapse. The scenario of SBSL is presented in Sec. III where the values of relevant parameters necessary for realizing the scenario are estimated. In Sec. IV we discuss the energy distribution functions of hot electrons and the breakdown conditions in strong flexoelectric fields as well as the spectrum of SBSL. In the Conclusion we summarize the results of our theory, discuss their relation to the experimental data, speculate about some possible modifications of the scenario, and point out some problems to solve.

II. FLEXOELECTRIC EFFECT AND ELECTRIC FIELD NEAR THE BUBBLE

We have already mentioned that the proposed mechanism of SBSL is based on the flexoelectric effect, namely, the appearance of a polarization (electric field) due to gradient of density (pressure) [14]. This effect is not widely known but was discussed briefly in Ref. [14]. In addition, the flexoelectric coefficients still have not been determined experimentally [15]. That is why we think it is worthwhile considering in more detail the appearance of electric field due to flexoelectric effect.

The flexoelectric effect is a particular case of a more gen-

eral phenomenon: appearance of electrical polarization \mathbf{P} as a result of the gradient of some scalar quantity, e.g., temperature, concentration of a component, mass density ρ . This effect should take place in any substance [16]. As usual, the material equation can be written in several forms. In particular, considering polarization as a function of dilatation $u = \Delta\rho/\rho$ and the electric field \mathbf{E} one has for an isotropic medium

$$\mathbf{P} = \alpha \nabla u + \varepsilon_0 \chi \mathbf{E}, \quad (1)$$

where χ is the electric susceptibility and α is one of the flexoelectric coefficients. We shall be interested in the case of spherical symmetry and the absence of free charges. In this case $\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = 0$. Then from Eq. (1) it follows that

$$\mathbf{E} = -\frac{\alpha}{\varepsilon \varepsilon_0} \nabla u = -\frac{\alpha \beta}{\varepsilon \varepsilon_0} \nabla p \equiv f \nabla p, \quad (2)$$

since $u = \beta p$, where p is the (excess) pressure, β is the compressibility.

To estimate the flexoelectric coefficients it is convenient to consider separately two main mechanisms of polarization: charge displacement and dipole ordering. We shall see that in both cases the coefficient of proportionality between polarization and gradient of pressure, f has the same characteristic value.

The charge displacement polarization is realized, e.g., in ionic crystals. When a gradient of dilatation takes place there are less and more compressed regions in each unit cell. The ions of larger radius tend to displace to the less compressed region while ions of less radius displace in the opposite direction. Since cations and anions usually have different radii their displacements produce polarization. The coefficient α can be estimated as follows [16]. The maximum (“atomic”) gradient of dilatation is equal to $1/d$, where d is the interatomic distance. This gradient has to produce “atomic” polarization $P_{\text{at}} \sim e/d^2$, where e is the electron charge, when the electric field is absent (compensated by some charges), i.e., $\alpha_{\text{ion}} \sim e/d$. Then from Eq. (2) it follows that

$$f \sim \frac{\alpha_{\text{ion}} \beta}{\varepsilon \varepsilon_0} \sim \frac{e \beta}{d \varepsilon_0}, \quad (3)$$

where we have taken into account that $\varepsilon \sim 1$ for ionic crystals.

We shall argue that the same estimation is applicable for materials with dipole ordering. The dipole ordering polarization in the absence of an external electric field but under a gradient of pressure arises because of geometric asymmetry of the molecular dipoles. For example, the geometric shape of water molecule is highly asymmetric. The negatively charged end is much more compact than the positive one. The negative charge is concentrated in the oxygen ion (O^{--}) while the positive charge is shared by two hydrogen ions (H^+) located fairly far from each other. Under a pressure gradient a water molecule tries to orient itself in such a way that the oxygen ion would be located in the region of higher density while the hydrogens would be located in the region of lesser density. In other words, a gradient of pressure leads to orientation of the water molecular dipoles. It is

well known that polarization due to dipole ordering is much more effective than polarization due to charge displacements. This is reflected in the fact that dielectric constants of dipolar materials are, normally, much larger than nonpolar materials. For the same reason it is natural to estimate $\alpha_{\text{dip}} \sim \varepsilon \alpha_{\text{ion}}$. Then from Eq. (2) it follows that for water

$$f \sim \frac{\alpha_{\text{dip}} \beta}{\varepsilon \varepsilon_0} \sim \frac{e \beta}{d \varepsilon_0} \sim 10^{-7} \frac{\text{V m}^2}{\text{N}}, \quad (4)$$

where we have taken into account that for water $\beta \approx 5 \times 10^{-10} \text{ m}^2/\text{N}$, $d \sim 10^{-10} \text{ m}$.

For what follows the sign of the flexoelectric coefficients is of importance. As has been mentioned above the negative tip of the water molecule, the oxygen ion, tends to be located in the region of higher pressure. This means that the polarization vector is directed opposite to the gradient of pressure, i.e., the flexoelectric coefficient α is negative and the coefficient f is positive.

Let us mention that we rather underestimated the flexoelectric coefficient of water than overestimated. Indeed, what we call α_{ion} is replaced, in fact, by α_{at} defining an “atomic” flexoelectric coefficient that is of the same order of magnitude for all substances, i.e., it does not take into account specific features of the substance in question. It is natural to expect that a substance consisting of molecules whose electric asymmetry (existence of a dipolar moment) is accompanied by a pronounced geometric asymmetry (as it is for water) will exhibit a stronger flexoelectric effect than that estimated above. However, while this coefficient is not measured (reliable calculations seem much more problematic than measurements) we shall assume the value given by Eq. (4). On the contrary, the conclusion reached about the sign of the coefficient f , which is crucial for the mechanism discussed in this paper, seems much more definite.

Above we have neglected the conductivity of water. This may seem questionable because the Debye radius of the electric field screening in water is comparable with the characteristic size of the strong field region ($\sim 1 \mu\text{m}$). However, this neglect is justified because, as a rule, the dielectric relaxation time τ_D is much greater than $\tau_c \approx 1 \text{ ns}$, which is the maximal characteristic time of the polarization change in our case. Increasing the ionic conductivity of water by adding, for example, NaCl, one can, according to our estimations, decrease τ_D down to 0.1 ns. In such an electrolyte the mechanism of SBSL discussed in this paper might be less effective.

III. SCENARIO: ESTIMATION OF THE MAIN PARAMETERS

The dynamics of bubble cavitation have been studied in many papers [2]. Here we will only discuss the short time interval when the bubble radius R is close to its minimum value R_c [Fig. 1(a)]. Figure 1(a) reflects the most essential features of Fig. 4 of Ref. [8] and Fig. 12 of Ref. [2] where experimental results were presented. Within this interval the velocity of the bubble surface $v = dR/dt$ reaches its maximum and reaches zero at the point $R = R_c$ [Fig. 1(b)] and the acceleration $a = d^2R/dt^2$ reverses its sign and can achieve huge values [Fig. 1(c)]. During the negative acceleration pe-

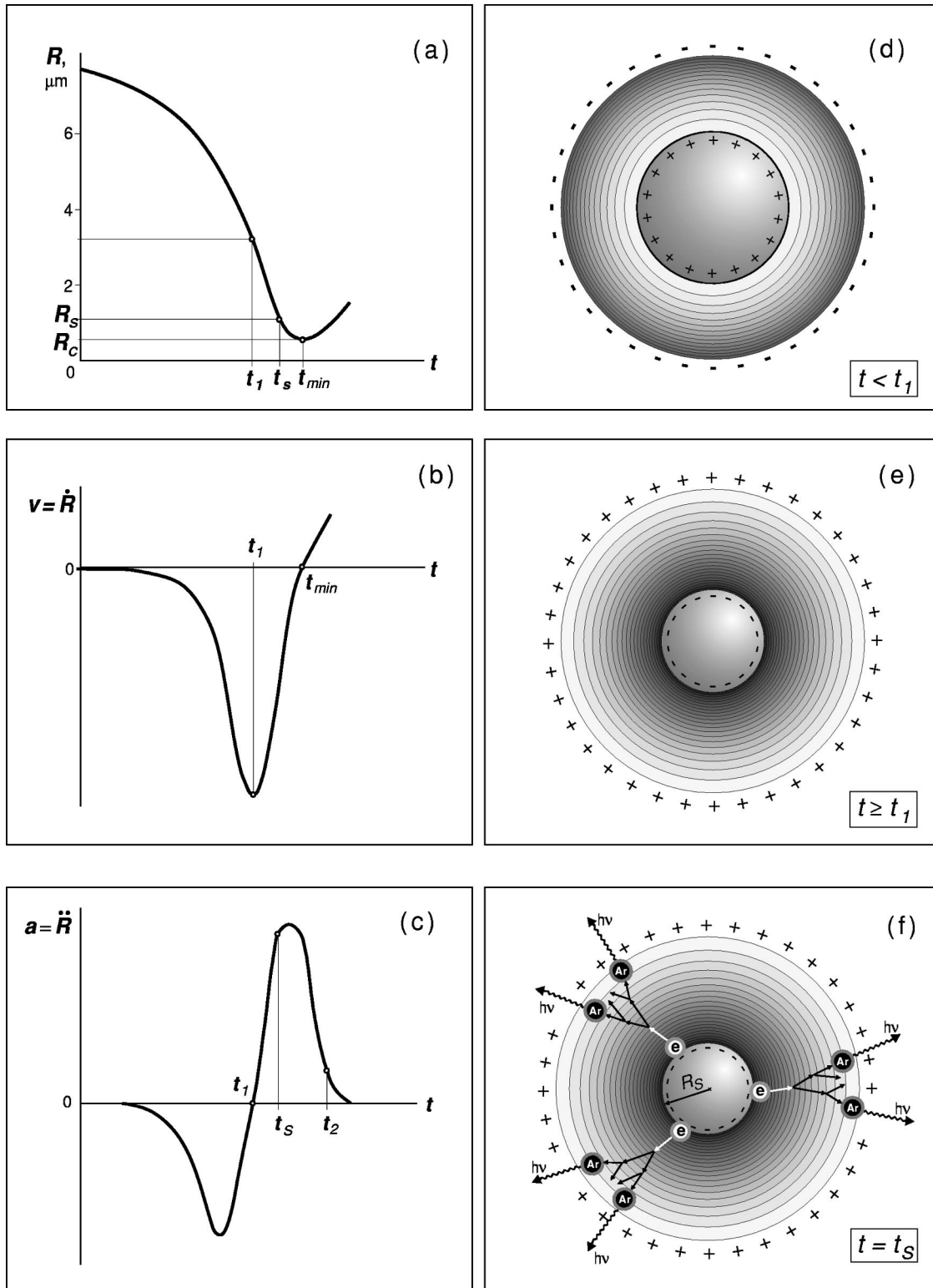


FIG. 1. Illustration of dynamics of the pulsating bubble and of formation of the flexoelectric field and the electric breakdown at the bubble collapse. Time dependence of the bubble radius (a), velocity (b), and acceleration (c) of the bubble surface. The flexoelectric polarization at different moments: (d) at the beginning of the collapse ($t < t_1$), (e) not very close to the turning point, (f) in the vicinity of the turning point ($R = R_C$).

riod [$t \sim t_1$, see Fig. 1(c)] the gradient of pressure $\nabla p = -\rho a$ is directed from the bubble center to its periphery, thus according to Eq. (4) the flexoelectric depolarizing field has the same direction [Fig. 1(d)]. That means that free electrons that could be generated in the gas or in water near the bubble

surface cannot be accelerated. During the positive acceleration period [$t_1 < t < t_2$, see Fig. 1(c)] the situation is opposite: the arising flexoelectric field is directed to the bubble center and the generated electrons can be accelerated by the field and produce a breakdown [Fig. 1(e)]. According to experi-

mental data [8,9] for a bright SBSL the characteristic value of the acceleration is about $(10^{11}-10^{13})$ m/s² during an interval, $\tau_c = t_2 - t_1 \sim 1$ ns, so the pressure gradient $\nabla p = -\rho a$ can reach $(10^{14}-10^{16})$ N/m³. Note that the gradient of pressure decays with distance from the bubble surface. For purpose of estimations one can consider water as incompressible liquid where $\nabla p = (\nabla p_s)R^2/r^2$, where ∇p_s is the gradient of pressure at the bubble surface. The same estimation for the gradient of pressure can be obtained if we take into account that the pressure is about (10^6-10^8) N/m² at the final stage of the bubble collapse and the extension of the high pressure region is about 1 μ m [2].

It follows from Eqs. (4) and (2) that for $\nabla p = (10^{14}-10^{16})$ N/m³ the value of the flexoelectric field E can reach (10^7-10^9) V/m. According to Eq. (4) the electric field decays just as the gradient of pressure, i.e., the flexoelectric field in water is given by the formula $E \approx E_s R^2/r^2$ where E_s is the field at the bubble surface, i.e., the radial extension of the strong field region is about 1 μ m. The field E , can essentially exceed the threshold field of dynamic electric breakdown of water E_{th} which is about $(1-3) \times 10^8$ V/m [18]. It does not mean, however, that electric breakdown will occur: a ‘‘lucky electron’’ which capable of provoking an avalanche is needed. A similar situation takes place with the laser breakdown [18]. At the same time the conduction electron concentration n in water at room temperature is practically zero ($n \sim 10^{-90}$ cm⁻³): water could be considered as a wide gap amorphous semiconductor with $E_g \approx 6.5$ eV [18,17,22–24].

The breakdown starts only the moment when the strong flexoelectric field is directed to the bubble center [Fig. 1(f)] and conduction electrons appear because of the sharp increase of temperature near the bubble surface. The latter takes place when the bubble radius $R \approx R_s$ which is close to $R_c \approx (0.5-1)\mu$. At this moment the flexoelectric field E_f may be much more greater than E_{th} so the coefficient of avalanche multiplication of an electron can be practically infinite and in this case just several electrons are enough to provoke the breakdown and to screen the field.

Let us show that even relatively moderate temperatures near the bubble surface (which seem to be generally acceptable for the regimes without the shock waves) are quite sufficient to provide a sufficient number of conduction electrons to ensure the breakdown. As in Ref. [6] we assume that the gas has the temperature of 7000 K. That means that the water layer with a thickness of the thermal penetration length, δ_T , has a temperature of about 3000 K. For δ_T one has

$$\delta_T = \left(\frac{2\kappa}{\rho c} t \right)^{1/2}, \quad (5)$$

where κ , the thermal conductivity of water is about 0.4 J/m s K; c , the specific heat, is about 4×10^3 J/m³ K; ρ , the density, is 10^3 kg/m³. Bearing in mind that the characteristic time for the last stage of the collapse is $\tau_c \sim 1$ ns [2], one finds that the thermal penetration length is $\delta_T \sim 0.1$ μ m. Following Refs. [17,18,24] we will consider water as an amorphous semiconductor with a band gap $E_g \approx 6.5$ eV and an effective density of states $N^* \approx 10^{21}$ for $T \approx 3000$ K. The equilibrium concentration of conduction electrons in water at

$T \geq 3000$ K is $n = N^* \exp(-E_g/2kT) \geq 3 \times 10^{15}$ cm⁻³. Taking into account that the volume of the hot surface layer is approximately $V \approx 10^{-12}-10^{-13}$ cm³ we find that the equilibrium number of conduction electrons in the layer is $N > 300-3000$. It is important also to find the time needed for the equilibrium concentration of electrons to be established. The thermal ionization frequency (see, e.g., Ref. [25]) is

$$\nu_T = (N^* \sigma v_T) \exp(-E_g/2kT), \quad (6)$$

where σ is the cross section of the free carrier recombination, v_T is the thermal velocity of conduction electrons in water. Taking into account that a reasonable value of σ is about 10^{-15} cm² and $v_T \sim 10^7$ cm/s we find from Eq. (6) that for $T > 3000$ K the transient time to the equilibrium $\tau_T = \nu_T^{-1} \leq 10^{-8}$ s. From that follows that during the characteristic time for the last stage of the bubble collapse $\tau_c \sim 1$ ns the number of conduction electrons in the layer N exceeds 30–300 electrons, which is quite enough to provoke breakdown.

Note that a similar number of free electrons can be generated by thermal ionization of the gas. Indeed, the assumed gas temperature (7000 K) is about two times larger than the temperature of the water and the ionization energy both of the water vapor and Ar, Kr, Xe is about 12–16 eV, i.e., also about two times larger than E_g . Authors of many works (see Ref. [2], and references therein) state that much higher temperatures can be reached because of shock waves forming in the bubble gas during the collapse. In principle, one can imagine a situation where high temperatures are not reached (and free electrons are not generated) before the shock waves are formed. In this case the shock wave, when it explodes, will start the electric breakdown.

As a result of breakdown the depolarizing flexoelectric field becomes screened. The total transmitted charge in the process of the screening is

$$Q_t = PS = 4\pi R_s^2 \varepsilon_0 E_s, \quad (7)$$

where we have taken into account that in our case $D = P + \varepsilon_0 E = 0$, i.e., $P = -\varepsilon_0 E$. Assuming $R_s \approx 1$ μ m and $E_s = (10^8-10^9)$ V/m we find that the maximum total number of transmitted electrons is $N_t = Q_t/e \approx (10^5-10^6)$.

Note that for considered electric fields the time of the screening (breakdown) τ_s is determined by the time it takes for the conduction electrons to cross the region of the strong electric field whose size is $l \sim R_s$. Thus $\tau_s = l/v_d$ where v_d is the electron drift velocity which in strong electric fields saturates at some value $v_d \approx 10^5$ m/s (see Sec. IV). Assuming $l \sim 1$ μ m we find $\tau_s \sim 10$ ps. Note that the value of τ_s is less than the observed SBSL pulse width [2,26,27].

The whole period of positive acceleration τ_c (see Sec. III) is about two orders of magnitude larger than τ_b . Therefore, after the breakdown is finished and the depolarization field is screened the polarization continues to change, because of change in acceleration. The electric field arises once more and can exceed the breakdown threshold. As a result a new breakdown will take place. Such a situation can be repeated several times. Effectively, it manifests itself in an increase of the pulse duration which may achieve a fraction of a nanosecond. Therefore, within our scenario the greater is the

pulse duration the greater is its energy. An analogous interrelation is observed in experiment [2,26,27].

IV. ENERGY DISTRIBUTION OF HOT ELECTRONS IN THE ELECTRIC FIELD AND SPECTRUM OF THE SONOLUMINESCENCE

We have already mentioned that the electric fields under consideration are very strong, inhomogeneous and change over time. However, the characteristic space and time scales of the field change are correspondingly $l \sim 1 \mu\text{m}$ and $\tau_c \sim 1 \text{ ns}$ and they are much more than the relaxation length λ and relaxation time τ_e of the hot electron energy which are, respectively, about $(10-100) \text{ \AA}$ and 10^{-13} s [17,18,24]. Therefore one can consider the local electron energy distribution function using well known results for homogeneous static electric fields [28-30].

The considered electric fields are superstrong, i.e., the following condition is valid:

$$qE\lambda \gg \hbar\omega_{\text{ph}} \equiv \epsilon_{\text{ph}}, \quad (8)$$

where ϵ_{ph} is the characteristic energy of local oscillations in water which is practically equal to the energy of optical phonons in ice, $\epsilon_{\text{ph}} \approx (80-100) \text{ meV}$ [17,18,24]. Using $\lambda \approx (10-100) \text{ \AA}$ one sees that the condition (8) is satisfied for fields $E > 10^7 \text{ V/m}$. Condition (8) means that in these fields an electron acquires, on average, an energy $qE\lambda$ which is much more than ϵ_{ph} . Since in the process of the acceleration an electron generates many phonons the electron energy distribution is nearly isotropic in the momentum space. Specifically, in this case the energy distribution of hot conduction electrons is approximated with high accuracy, up to energies of electrical breakdown $\epsilon = E_g$, by the Maxwell function [28-30]

$$f(\epsilon) \sim \exp\left(-\frac{\epsilon}{kT_e}\right) \quad (9)$$

with an effective electron temperature T_e which is determined by the balance equations for energy and momentum of the hot electrons

$$\frac{d\epsilon}{dt} = eEv_d - \frac{\epsilon_{\text{ph}}v_T}{\lambda} = 0, \quad (10)$$

$$\frac{dp}{dt} = eE - m_e v_d \frac{v_T}{\lambda} = 0, \quad (11)$$

where v_T is the effective thermal velocity of electrons. Since for the Maxwell distribution

$$\frac{3}{2}kT_e = \frac{1}{2}m_e v_T^2, \quad (12)$$

from Eqs. (10)–(12) it follows that

$$v_d = \sqrt{\epsilon_{\text{ph}}/m_e} \quad (13)$$

and

$$kT_e = (eE\lambda)^2/3\epsilon_{\text{ph}}. \quad (14)$$

From Eqs. (12) and (13) as well from Eq. (8) one sees that $v_T/v_d = \sqrt{kT_e/\epsilon_{\text{ph}}} = qE\lambda/\epsilon_{\text{ph}} \gg 1$. This is precisely the condition of validity for the thermalization of the hot electrons and use of the Maxwell distribution.

Conduction electrons in water form polarons which are conventionally called hydrated electrons [22,24]. However, in the strong electric field the polaron states decay and the current carriers are the usual conduction electrons. For purpose of estimation we assume that their effective mass m_e is close to that of free electrons m_0 . Then from Eq. (13) it follows that $v_d \approx 10^5 \text{ m/s}$ for $\epsilon_{\text{ph}} \approx 100 \text{ meV}$. It has already been mentioned that the electric fields under consideration are $E \approx (10^8-10^9) \text{ V/m}$. It follows from Eq. (14) that for such fields $kT_e \approx (1-10) \text{ eV}$, i.e., $T_e \approx (10^4-10^5) \text{ K}$ for $\lambda \approx (10-100) \text{ \AA}$. One sees that the electron temperatures can be several orders higher than the gas temperature in the bubble. Recall that for our scenario (see Sec. III) it sufficient that the gas temperature be about 7000 K.

Now we will discuss the role of noble gases dissolved in water. An important feature of a noble gas atom is the existence of metastable states. The life time of the metastable states can reach several milliseconds when the noble gas atoms are impurities in solids (see, e.g., Refs. [20,21]). Since the nearest order in water is essentially the same as in solids it would be natural to expect that the life-time of the metastable states for the noble gas atoms in water is not less than 1 ns. Hot electrons not only generate new conduction electrons (the breakdown avalanche) but also excite the noble gas atoms into metastable states. Below we will estimate from the experimental data that the characteristic value of $kT_e \approx (2-5) \text{ eV}$. However, a considerable number of electrons may have energies about 10 eV and can excite the noble gas atoms.

Note that the energies necessary for excitation to the metastable states ϵ_m for Xe, Kr, Ar, Ne, He are about 10 eV and increase monotonically from Xe to He. In other words, it is much easier to excite Xe, Kr, and Ar than Ne and He. This could be the reason for the increase in SBSL intensity in the series He-Xe, which has been observed experimentally [2,31].

As we have mentioned above, the lifetime of the metastable states of noble gas atoms in water is expected to be fairly long. Thus, once excited a noble gas atom can remain in a metastable state for the entire time interval of positive acceleration and multiple breakdowns, $\tau_c \sim 1 \text{ ns}$. The major part of electrons has the energies $\epsilon < \epsilon_m, E_g$; they collide with these metastable atoms and transfer them to higher excited states. The radiation transitions between high-energy excited states of noble gas atoms govern the SBSL spectrum.

Note that the lifetime of the metastable states can exceed the period of the acoustic wave. In this case there will be an effect of accumulation of the noble gas atoms in metastable states resulting in the gradual build up of the SBSL power during several periods of the acoustic wave.

A specific feature of a noble gas is an abundance of excited states with energies higher than those of metastable states and with high probabilities of the radiation transitions between them. That is why the optical spectra of the noble gas atoms contain many lines [20,21]. Because of the Stark effect in the strong electric field these lines are split. In addition, in the active region the strong electric field changes at

least several times and the observed radiation spectrum is a superposition of the spectra of the atoms in different strong electric fields. In other words one can consider the density of the atomic excited states as a constant.

The probability of a hot electron having an energy $\varepsilon < E_g$ is given by Eq. (9) and at every collision it transfers the noble gas atom in a metastable state to a state with energy ε , the reference point of energy being the energy of the metastable state (for our estimations we consider only one metastable state). The concentration of atoms excited during the time of a single electric breakdown, i.e., the screening time τ_s to energies within an interval $d\varepsilon$ reads

$$dn_n^{**} = n_n^* (\sigma_{ex} v_T n) \tau_s \exp\left(-\frac{\varepsilon}{kT_e}\right) \frac{d\varepsilon}{kT_e}, \quad (15)$$

where n_n^* is the number of the noble gas atoms in the metastable state, σ_{ex} is the cross section of the impact excitation of an atom from the metastable state to a state with energy ε . Atoms excited to states with the energy ε generally do not go to the ground state directly but through intermediate excited states. It reasonable to assume that with a high probability they radiate phonons with energy $h\nu \approx \varepsilon$. So the spectral density of the SBSL radiation energy per pulse for unit volume can be written as

$$\tilde{P}(h\nu) d(h\nu) = h\nu w_r n_n^* (\sigma_{ex} v_T n) \tau_s \exp\left(-\frac{h\nu}{kT_e}\right) \frac{d(h\nu)}{kT_e}, \quad (16)$$

where w_r is the probability of the spontaneous radiation transition. Taking into account that $w_r = [4(2\pi)^4 \nu^3 / 3c^3 h] D^2$ where D is modulus of matrix element of the dipole moment of the transition [32] we find

$$\begin{aligned} \tilde{P}(h\nu) d(h\nu) &= \frac{4(2\pi)^4 D^2}{3c^3} n_n^* (\sigma_{ex} v_T n) \tau_s \nu^4 \\ &\times \exp\left(-\frac{h\nu}{kT_e}\right) \frac{d(h\nu)}{kT_e}. \end{aligned} \quad (17)$$

Recall that T_e in Eq. (17) is a function of the coordinates because $T_e \sim E^2$ [see Eq. (14)]. Putting, as before, $E = f\nabla p \approx E_s R_s^2 / r^2$ and integrating approximately Eq. (17) we find the spectral power of SBSL for a single breakdown is

$$\begin{aligned} P &= \int \tilde{P}(h\nu, r) dV = \frac{4(2\pi)^4 D^2}{3c^3 h} n_n^* (\sigma_{ex} v_T N_t) \tau_s \nu^3 \\ &\times \left[1 + \frac{kT_{es}}{h\nu} \exp\left(-\frac{h\nu}{kT_{es}}\right) \right], \end{aligned} \quad (18)$$

where $kT_{es} = (eE_s \lambda)^2 / 3\varepsilon_{ph}$ and N_t is, practically, the total number of electrons participating in the breakdown. Note that the approximative Eq. (18) is not sensitive to the form of decay of the field, it is important only that E decays more steeply than r^{-1} , i.e., it is not important that for ∇p we use an expression for an incompressible liquid.

The observed spectra are cutoff in the shortwave region because of the absorption of water. This can be taken into account by multiplying Eq. (18) by $\exp[-\alpha(h\nu)L]$, where L

is the size of the acoustic resonator ($L \approx 2.5$ cm [2]). Because of the Urbach absorption tails [17,23] the radiation maximum is located considerably below than $h\nu \approx E_g \approx 6.5$ eV.

It should be emphasized that the spectrum given by Eq. (18) resembles the black-body spectrum but temperature is given here by the effective temperature T_{es} of hot electrons near the bubble surface. The value of T_{es} may be much higher than the bubble gas temperature. Experimentally observed spectra can be fitted, in the wavelength interval (200–700) nm, to the black-body ones with temperatures $(2-5)10^4$ K [2,33]. According to Eq. (14) such electron temperatures are reached at electric fields $E_s \approx (2-10)10^8$ V/m for values of $\varepsilon_{ph} \approx 0.1$ eV and $\lambda \approx (10-100)$ Å characteristic for water [18]. As follows from Eq. (4) and $\nabla p = -\rho a$ such fields are realized at accelerations $a \approx (10^{13}-10^{14})$ m/s². Similar accelerations are reported in Refs. [2,9].

Integrating Eq. (18) multiplied by $\exp[-\alpha(h\nu)L]$ we find an estimate of the radiation energy for a single breakdown

$$\begin{aligned} W_r &= \int P w_r^{-1} \exp[-\alpha(h\nu)L] d(h\nu) \\ &\approx (\sigma_{ex} v_T N_t) \tau_s n_n^* h \bar{\nu} \approx \frac{\nu_T}{\nu_d} (\sigma_{ex} R_s n_n^*) N_t h \bar{\nu}, \end{aligned} \quad (19)$$

where $h\bar{\nu}$ is the characteristic photon energy which is close to the energy of the maximum of the observed spectrum, which is about (5–6) eV in the case of strong electric field of our interest. Recall that in Eq. (19) $\tau_s \approx R_s / \nu_d$ is the screening (breakdown) time and $N_t \approx 4\pi R_s^2 \varepsilon_0 E_s / e$ is the number of transmitted electrons in the screening process (Sec. III) and n_n^* is the concentration of noble gas atoms in a metastable state near the bubble surface.

As we have mentioned before it was shown in Refs. [3,4] that because of dissolved gas diffusion and chemical reactions an accumulation of noble gas in the bubble takes place while the bubble pulsates and in stationary conditions the gas in the bubble consists almost entirely of noble gas. Therefore one can assume that the concentration of the noble gas atoms n_n near the bubble surface is close to its saturation value. Note that this value has to be estimated for atmospheric pressure and ambient temperature rather than for the high pressures and temperatures existing at the last stage of the collapse over a very short time. This is why we assume that $n_n \approx (10^{18}-10^{19})$ cm⁻³. Now we will argue that the value of n_n^* can be only one order of magnitude less than n_n . Indeed, for $kT_e \approx (3-5)$ eV obtained above by fitting the SBSL spectrum to the black-body spectrum, the number of electrons having an energy higher than 10 eV, N_h may be about $10^{-3}-10^{-2}$ of the total electron number $N_t \approx 10^6$, i.e., N_h is about 10^3-10^4 . Such a ‘‘superhot’’ electron excites a noble gas atom to the metastable state over the time $\tau_{ex} = (\sigma_{ex} v_T n_n)^{-1} \approx 10^{-12}$ s for $\sigma_{ex} \approx 10^{-15}$ cm², $v_T \approx 10^6$ m/s and $n_n \approx (10^{18}-10^{19})$ cm⁻³. Therefore a ‘‘superhot’’ electron during its participation in screening excites τ_s / τ_{ex} noble gas atoms and the total number of the excited atoms is $N_h \tau_s / \tau_{ex} \approx 10^4-10^5$ if one takes into account that $\tau_s \approx 10\tau_{ex} \approx 10^{-11}$ s. The total number of the noble gas at-

oms in the region of the strong field ($\sim 1 \mu\text{m}^3$) is about 10^6 – 10^7 , i.e., the percentage of the noble gas atoms excited to the metastable state during a single breakdown can be about 10%. Since the lifetime of the metastable state is much more than τ_c and during this time interval several breakdowns can take place (Sec. III), one may expect that the number of the noble gas atoms excited to the metastable state during the interval τ_c is only one order of magnitude less than the total number of these atoms, i.e., $n_n^* \sim 10^{18} \text{ cm}^{-3}$. If the lifetime of the metastable states exceeds the acoustic period ($\sim 30 \mu\text{s}$) an accumulation of noble gas atoms in the metastable states can also occur during several acoustic periods.

Now we can estimate the total radiation energy. We have mentioned above that the maximum value of $N_t \approx 10^6$, $R_s \approx 1 \mu\text{m}$, $\sigma_{ex} \approx 10^{-15} \text{ cm}^2$, and $v_T \gg v_d$. Taking into account that the positive acceleration period $\tau_c \sim 1 \text{ ns}$ and the breakdown time τ_s is about 0.01 ns one can assume that the number of breakdowns is not less than 10. Thus one finds from Eq. (19) that the maximum photon number in the SBSL pulse can be more than 10^7 . This value corresponds to the maximum photon number observed experimentally [2,33,34]. Note that the radiation energy is a small part of the total energy of the flexoelectric field (see Ref. [35]).

V. CONCLUSIONS

Let us emphasize once more that within the mechanism of SBSL considered the main processes occur in water near the bubble surface unlike the most widely discussed mechanisms of SBSL [2]. Within the framework of this mechanism many experimental data about the SBSL can be explained quite naturally. Of course, since the parameters of the collapsing bubble are not reliably known when the bubble radius is close to its minimum value we can present no more than order-of-magnitude estimations.

Let us summarize the main results.

(i) The minimum duration of the SBSL flash is determined by the single breakdown (screening) time, $\tau_s \approx 10 \text{ ps}$. A larger time is possible because of the multiplicity of breakdowns. The maximum duration is limited by $\tau_c \sim 1 \text{ ns}$. The longer is the duration the greater is the energy of the flash. This is in agreement with experiments where it was found that the pulse duration changes from 30 ps to 400 ps when its energy increases [2,26,27].

(ii) According to our estimations the maximum energy of the flash corresponds to 10^7 – 10^8 photons with energy (5–6) eV, which also agrees with the experiment [2,33,34].

(iii) Within our scenario the noble gas atoms play an important role. They do not reduce so much the breakdown threshold as they govern the radiation process. Abundance of optical transitions in these atoms and inhomogeneous broadening because of the Stark effect explain the practically continuous character of the SBSL spectrum.

(iv) In agreement with the experiment [2,33] the theoretical spectrum of the SBSL resembles the black-body spectrum but the temperature is given here by the effective temperature of the hot electrons which can be about several eV, what corresponds to the observed apparent radiation temperature [2,33]. At the same time the gas temperature is not

directly related to the radiation temperature and can be considerably less than 1 eV.

(v) The increase of influence on SBSL intensity in the noble gas series He-Xe observed in the experiment [2] is connected with the decrease, in this series, of the energy of the lowest metastable state.

(vi) The pulse width does not depend on the spectral range of the radiated photons. This also agrees with experiment [26].

(vii) The effect of synchronization of the light pulses observed experimentally [2,19] is explained.

Note also that within our scenario of SBSL the influence of magnetic fields on SBSL is fairly weak. Their influence becomes appreciable when they are high enough to hamper the heating of electrons [36]. This might be the reason for the decrease of the SBSL intensity in strong magnetic fields which has been observed experimentally [37].

It seems that the considered mechanism of SBSL is especially effective for water because of a lucky coincidence of several conditions.

(i) The strong geometric asymmetry of the water molecule, which accompanies its electric asymmetry, provides the needed sign of the flexoelectric coefficient. This sign is such that the electric field has the ‘‘correct direction’’ (accelerates electron) over the same (very short) period in which electrons are generated because of the sharp increase of the bubble gas temperature. The temporal coincidence of these two circumstances is a possible reason of the effect of synchronization of the light pulses observed experimentally [2,19].

(ii) Water is a semiconductor with a relatively narrow band gap ($E_g = 6.5 \text{ eV}$) and sufficiently wide conduction band, what is necessary for the heating of the electrons in strong electric field.

(iii) High solubility of noble gases in water what makes possible high concentrations of noble gas in water near the bubble filled by the noble gas accumulated there in the process of the bubble pulsations.

Fulfillment of these conditions gives the answer to the question why water is the friendliest liquid for SBSL [2].

Some experimentally found characteristics of SBSL have not been explained in this paper, in particular the dependence of the energy of the pulse upon the partial pressure of noble gases and water temperature [2]. These dependences may be not necessarily a manifestation of the radiation processes studied in this paper but they could be a consequence of a set of various factors. They may be determined by the hydrodynamics of the pulsating bubble, the solubility of noble gases in water and also by the temperature dependence of the flexoelectric coefficient of water which still remains, unfortunately, unmeasured.

Although the main features of SBSL seem to be explainable within our scenario, these explanations are qualitative rather than quantitative. We are still a long way from a quantitative theory at present. One of the main aims of the paper is to stimulate some experiments that could either support or discard the proposed mechanism of SBSL.

(i) Measurements of flexoelectric coefficients of water.

(ii) A detailed study of radiation spectra at electric breakdown of water and ice with different concentrations of noble gases.

(iii) Study of influence of water conductivity on the SBSL intensity.

After performing these experiments it makes sense to develop the theory further. In particular, it will be necessary to study in more detail the kinetics of the screening process and of the excitation of noble gas atoms while taking into account the time variation of the distribution function of the hot electrons. This problem should be considered together with that of the determination of the spatial distribution of excited noble gas atoms near the bubble surface. Diffusion and relaxation of the excited atoms should be considered together, of course, with the processes that lead to noble gas accumulation in the bubble [3,4].

In our estimations we assumed that flexoelectric coefficient of water has its “natural” value. This was sufficient for

the theoretical estimations to be in agreement with the experimental data. In fact, because of the abovementioned strong geometric asymmetry of the water molecule, the coefficient could be even larger. If this is the case some new phenomena will take place including influence of the flexoelectric effect on hydrodynamics of the pulsating bubble and x-ray radiation induced by electrons of very high energy.

ACKNOWLEDGMENTS

We are grateful to V. Kholodnov for useful discussions. N.G. and V.V.O. thank EU ESPRIT, the Spanish CSIC, and NATO for Linkage Grant Ref. No. OURLG 970308. Also, A.P.L. thanks NATO for Linkage Grant No. HTECHLG 971213.

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