On the Mechanisms of Sonoluminescence in Polar and Nonpolar Liquids

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Abstract—The results of the estimation of the strength of the electric field that is formed in polar liquid near the liquid–gas interface of a collapsing gas bubble are presented. A double electric layer and flexo- and thermoelectric effects are considered as field sources. It is shown that the field strength in water can reach 10^9 V/m, and the dimensions of the strong field area can be up to several tens of micrometers. These results are an argument for the earlier made assumption that there may be two sources of luminescence in polar liquid–gas systems: adiabatically heated gas inside the bubble and channels of electrical breakdowns in the liquid. In the case of nonpolar liquid, no second source is formed. The experiment for testing the model is proposed.

INTRODUCTION

Two models are used in the study of sonoluminescence (SL), which is a phenomenon of pulsed light emission by collapsing gas bubbles (steam, steam–gas mixture) in a liquid exposed to a periodic acoustic influence: the model of the bubble dynamics and the model of the emitter formation. The dynamics model is the most developed: it describes precisely the experiment during 99.5% of the acoustic cycle [1–3].

The models of the emitter formation mechanism (hereinafter, SL models) have been less successfully developed. Since the SL was discovered, quite a few models have been offered. With some exceptions, they can be roughly divided into two groups: thermal and electric. In each of them, a certain high-temperature zone is the source of emission. The terms "thermal" and "electric" indicate the supposed mechanism of formation of such a zone. The thermal models are based on assumptions of the gas heating method. In the electric models, plasma in the breakdown channel in gas or liquid is the source of emission. Most of known models are considered in the reviews [1–5], where the results of the model analysis are given, and the failure of some of them are shown. Two thermal models are most commonly used today to explain the results of experiments: the unshocked compression model (UCM) and the shock wave model (SWM).

Within UCM, the source of emission is an adiabatically compressed gas inside the bubble with the temperature of ∼1 eV and density ∼1 g cm^{-3} [3]. The dimensions of the high-temperature zone coincide with the minimum dimensions of the bubble. Within the SWM, the hot zone is formed due to reflection from the center of a spherical shock wave that is formed in gas at the stage of bubble compression, when the wall velocity becomes higher than the Mach number. The zone radius is smaller than 0.1 Rc (Rc is the minimum radius of the bubble). The source of emission is plasma with the density of ∼10 g cm^{-3} and temperature up to 10 keV [6, 7].

Some electric models are based on the assumption that bubble collapse is asymmetric, which causes the formation of jets of liquid or gas. In [8], spark discharges around the water jet are the light source; in [9], this role is played by electric discharges in cracks, which are formed in water when a gas jet collides with the bubble wall. In the model [4, 10] developed for a multibubble SL, the source of emission is the channel of electric breakdown in gas; here, the electric field is generated by bubble deformation in the acoustic field. In [11, 12], authors supposed that photons were emitted by noble gas atoms dissolved in water, which were transformed into excited states by electrons accelerated in the near-surface water layer by the electric field

generated by the flexoelectric effect. In [13, 14], a polarization model (PM) was proposed based on the assumption that there were two sources of emission: thermal and electric. The first source was the adiabatically heated gas inside the bubble, and the second source was the electric breakdown channels in the liquid. The electric source occurs only in polar liquids.

In [5], SL models were tested by the results of experiments. It is shown that PM gives quite a satisfactory qualitative explanation of the whole set of known experimental data.

In this paper, in terms of the development of ideas about the electric source of PM, the electric field strength is estimated in near-surface layer of the polar liquid at the bubble collapse. A double electric layer (DEL) is considered as the source of the field: a thin surface layer of spatially separated electric charges of opposite signs formed in the vicinity of the interface between two phases [15], and polarization of the liquid under the pressure gradient (flexoelectric effect (FE) [16]) and temperature gradient (thermoelectric effect (TE) [17, 18]). An experiment to verify the polarization model is proposed.

1. ELECTRIC EFFECTS IN POLAR LIQUID

We consider the conditions of DEL formation and the possibility of FE and TE manifestations during the acoustic cycle of the bubble.

We choose, for certainty, the water–air system; the experiment in this environment at the frequency of acoustic field $f_a = 26$ kHz and its amplitude $p_a = 1.3$ atm under normal initial conditions is described in [1]. In accordance with [1], we consider several stages of the acoustic cycle (~38 μs) along the curve of the time dependence of the bubble radius $R(t)$ in the steady-state mode:

—the stage of relatively slow bubble expansion as a response to the acoustic field rarefaction ($t_1 \approx 15$ μs);

—the stage of reaching the maximum radius R_m due to the bubble inertia ($t_2 \approx 5$ μs);

—the collapse stage (time of compression from $0.5R_m$ to the minimum radius R_c, $t_c \approx 0.5$ μs);

—bubble oscillation stage near the equilibrium state with radius R_0 (period $t_D = 1$ μs).

By order of magnitude, the bubble radius at different stages of the acoustic cycle is $R_c \approx 0.5$ μm, $R_0 \approx 5$ μm, and $R_m \approx 50$ μm. At the final stage of collapse ($R_0 \rightarrow R_c$), the bubble wall speed can reach ~4 M (M is the Mach number). At this stage (duration 5–10 ns) a light flash is generated and a shock wave is formed in the liquid [1].

Thus, the bubble dynamics is essentially nonlinear in the range of acoustic pressure values, in which SL is observed. The dependence $R(t)$ acquires a characteristic form with relatively slow expansion and rapid compression (collapse). According to the literature [3, 5],

a single-bubble sonoluminescence (SBSL) was observed at the frequencies f_a in the range of 10 kHz–1 MHz, i.e. the acoustic cycle period was 1 μs or more.

In the example above, the expansion stage of the bubble lasts about a half of the acoustic field period. We assume that this relation is true for all values of p_a and f_a, for which SBSL is observed. DEL starts to form in this system from the moment the bubble forms and thus the interfacial surface: liquid–vapor or the liquid–vapor–gas mixture (if gas is dissolved in liquid) appears. At the stage of bubble expansion, the pressure drop in water is about 1 atm, and its density is almost constant. The above data show that at the expansion stage, DEL will be formed in a thermodynamically quasi-equilibrium state.

At the compression stage, a high-pressure zone is formed in liquid near the bubble wall. This is shown, for example, in [19], where a resonator that allowed experiments at static pressures up to 300 atm was used to study the SBSL. In experiments with large bubbles ($R_{max} = 1.4–9$ mm) formed in water by optical breakdown, dark areas around the collapsing bubble were recorded using a high-speed camera. The authors attributed this result to the formation of a high-pressure zone with a large gradient and thus an increase in light reflection coefficients (experiments were carried out with backlighting). The outer edge of the area is quite distinct; its diameter is ~1 mm. As the bubble radius decreases, the pressure and gradient increase and the area becomes darker. After the collapse, the inner boundary of the area starts to move away from the collapse zone, eventually forming a shock wave (SW) in liquid [19].

The shock wave in liquid is also formed at $p_0 = 1$ atm. For these conditions, the dimensions of the region of gradient existence are estimated based on the results of the SW registration experiments. In [20], for a water–argon system under normal initial conditions and $p_a = 1.28–1.39$ atm, it was shown that the fully formed SW was recorded at the distance $r \geq 2.5$ μm from the center of the bubble with an amplitude 38–60 kbar at $r = 2.5$ μm and a decay that is faster than r^{-1}. Assuming that SW is formed in the region of pressure gradient, it is possible to estimate the dimensions of this region as 1–2 μm.

To estimate the pressure gradient, it is necessary to know the pressure on the bubble wall p_w in a liquid. We assume that the pressure p_w is equal to the gas pressure p_g inside the bubble and use the calculated data for this value, known from the literature [20–22]. In [20], the values $p_g = 35–60$ kbar were obtained at $p_a = 1.28–1.39$ atm for the water–argon system, which was in good agreement with the pressure at the SW front in water registered in this work.

In [21–24], the authors calculated thermodynamic parameters of gas (temperature T_G and pressure P_G) and degree of its ionization α_G for different systems:

Table 1. Values at maximum compression of the bubble

Liquid	Gas	R_c/R_0	T_G, K	p_G, GPa	α_G	References
Water	Ar	0.141	17130	3.99	9×10^{-3}	[21]
	N_2	0.105	4470	6.62	1.5×10^{-10}	[22]
	N_2 + 1% Ar	0.105	4550	7.11	2.3×10^{-10}	
	N_2 + 10% Ar	0.107	5300	6.81	5.5×10^{-9}	
	Ar*	0.100	14500			[23]
	Air*	0.140	6400			
	Ar**	0.150	19000		7×10^{-3}	[24]

* f_a = 30 kHz, ** f_a = 26.4 kHz, R_0 = 4 μm, p_a = 1.47 atm.

water–Ar [21–24], water–N_2 [22], and water–N_2/Ar mixtures [22]. In [21, 22], the Rayleigh–Plesset equation with Keller corrections [3] was solved to determine the dynamics of the bubble at the following parameters: p_0 = 1 atm, p_a = 1.4 atm, f_a = 25 kHz, R_0 = 5 μm, and T_0 = 293 K. The calculation results are presented in Table 1.

Note that the data obtained by different authors for the water–Ar system are in satisfactory agreement.

Based on these data, we assume for estimation that p_w = 1–10 GPa for the range ρ_a = 1.1–1.5 atm (water systems and normal initial conditions) that is typical of the SBSL study. In this case, the pressure gradient is estimated at 10^{15}–10^{16} Pa/m.

On the other hand, as noted in [7] with reference to [25, 26], the pressure in an uncompressed liquid (p_0 = 1 atm) near the wall of a collapsing bubble can exceed 100 GPa with the corresponding rise in temperature of just a few degrees in the adiabatic compression assumption. In this case, the gradient is estimated at ~10^{17} Pa/m. The formation of a pressure gradient zone should cause a flexoelectric effect.

The bubble compression is accompanied by an increase in gas temperature. At the maximum compression, it can reach significant values. This follows from the results of numerical modeling (Table 1) and from the results of temperature determination by measured emission spectra [1, 3, 5]. At the last stage of the collapse, which duration is ~1 ns, the liquid layer can be heated by gas. We estimate the water temperature based on the calculated temperature of gas (Ar, N_2) presented in Table 1, using the following approach.

We consider the bubble as a pulse source of a thermal wave with the duration of 0.5 ns and the amplitude of 0.5 T_{max}. According to the solution of the problem for instantaneous point source in the case of linear temperature conductivity [27], the penetration depth of the wave r can be estimated as follows:

$$r \sim (4Xt)^{1/2},$$

where X is the thermal diffusivity and t is the time.

Assuming that X = 1.5 × 10^{-7} m² s⁻¹ for water under normal conditions [28], we have $r \sim 2 \times 10^{-8}$ m. Considering that the temperature decreases e times at this distance and using the data from Table 1 we obtain the water temperature at a distance r from the interface:

—$T_w \approx$ 3000 K for the water–argon system and

—$T_w \approx$ 800 K for the water–nitrogen system.

In the order of magnitude, the temperature gradient in the heated water layer is 10^{11} K/m. The gradient creates the grounds for manifestation of the thermoelectric effect.

The review has shown that DEL can be formed during the acoustic cycle of the bubble, and the conditions for the FE and TE manifestation are created. We consider these effects as potential sources of electric field in liquid at the stage of bubble compression.

2. ELECTRIC FIELD IN LIQUID

2.1. Double Electric Layer at the Liquid–Gas Interface

There are a variety of different methods of studying the structure and characteristics of DEL, and models have been proposed for its description [29]. Many studies have been carried out for metal–electrolyte systems. However, much less data has been obtained for liquid–gas systems, our area of interest. Below, we present data from the literature data the water–air system DEL under normal conditions.

The literature offers no single point of view on the structure of DEL. The most commonly used model is based on a double electric layer that consists of a Helmholtz layer, which is a layer of oriented dipoles adjoining the interface, and a diffusion layer, which is formed under the influence of the field of oriented dipoles composed of H^+ and OH^- ions [30]. The orientation mechanism varies from author to author: in [31], it is a dipole–quadrupole interaction; in [15], within the quantum-statistical approach, it is fluctuation polarization caused by thermal motions of molecules; and in [32], it is the asymmetry of the force field in a liquid–gas transition layer.

According to [15, 30, 33], dipoles are oriented so that O^- ions are directed outwards and H^+ ions are directed inwards the liquid. With this orientation, the jump in potential at the interface is positive. According to other data [32], there is no consensus on the sign and value of the jump in potential: it varies from +0.5 V to −1.1 V among different authors. This suggests, in the first place, an insufficient development of methods of its definition. There are also discrepancies in the number of oriented molecules. In [15, 31], all molecules of the surface are oriented, while in [30] only three to four percent of molecules are oriented.

The above information shows that the DEL has not been studied sufficiently; the data on it are often contradictory. For further evaluation, we use the DEL characteristics, which most authors adhere to:

—DEL consists of a Helmholtz layer and a diffusion layer. The thickness of the Helmholtz layer is equal to the length of the OH bond of a water molecule, and the diffusion layer thickness is ≤ 1 μm under normal conditions [34];

—in the Helmholtz layer, the dipole moments of all molecules of the surface are oriented perpendicular to the interface with oxygen ions directed towards gas.

The mechanism of DEL evolution at the stage of bubble compression is proposed in [35]. According to this work, when the surface area of the bubble decreases, the number of oriented molecules in the surface layer decreases. Let us estimate this effect for the above case: $R_{max} = 50$ μm, $R_{min} = 0.5$ μm.

At R_{max}, water is under normal conditions, its density $\rho_0 = 1$ g cm^{-3}, and the volume and surface densities of its molecules are $N_v = 3.3 \times 10^{22}$ cm^{-3} and $N_s \simeq 10^{15}$ cm^{-2}, respectively. The bubble surface $S_{max} = 3 \times 10^{-4}$ cm^2 and, consequently, the surface layer consists of $N_m = N_s S_{max} = 3 \times 10^{11}$ water molecules. If this amount is conserved during the collapse, then the density at R_{min} ($S_{min} = 3 \times 10^{-8}$ cm^2) should be $Ns_{min} \simeq 10^{19}$ cm^{-2}. However, as shown earlier, a high-pressure zone with a large gradient is formed around the collapsing bubble. The pressure is 3−6 GPa in this zone at normal initial conditions and $p_a \approx 1.3−1.4$ atm [20]. In the shock-wave compression experiments, it is shown that water density at such pressures is $\rho_p = 1.45−1.59$ g cm^{-3} [36]. If we take the value $\rho_p = 1.5$ g cm^{-3} for the estimates, the surface density of molecules is $Ns_{min} = 1.5 \times 10^{15}$ cm^{-2}, $N_m = 4.5 \times 10^7$ molecules. This means that during collapse, about 10^{11} molecules should be pressed out from the surface layer and distributed in the volume according to the created density gradient that corresponds to the hypothesis [35]. At the final stage of the collapse with the duration equal to the time of orientation relaxation τ_d, the molecules displaced from the surface layer retain the dedicated direction, i.e. a cloud of oriented molecules is formed. For evaluation purposes, it can be presented as a spherical capacitor with a distance L_p between its plates:

$$L_p = \int_{t_{R_c}-\tau_d}^{t_{R_c}} V(t)dt = \bar{V}\tau_d, \qquad (1)$$

where t_{R_c} is the time moment, when the minimum radius is reached, and V is the bubble wall velocity.

In formula (1), τ_d is the characteristic time of the collective relaxation process (macroscopic relaxation time).

We evaluate it using the Debye formula [37]:

$$\frac{\tau_d}{\tau_s} = \frac{\varepsilon + 2}{\varepsilon_\infty + 2}, \qquad (2)$$

$$\tau_s = \frac{4\pi a^3 \eta}{kT}, \qquad (3)$$

where τ_s is the reorientation time of a dipole; ε and ε_∞ are the static and high-frequency dielectric permittivities; a is the molecule dimension, η is the dynamic viscosity; k is the Boltzmann constant; and T is the temperature.

In [38], the values $\tau_d = 8.5$ ps and $\tau_s = 1$ ps were obtained for water by the method of frequency dielectric spectroscopy at $T = 298$ K and normal pressure; their ratio $\tau_d/\tau_s = 8.5$. The calculation of formula (2) at $\varepsilon = 78.25$ [39] and $\varepsilon_\infty = 6.3$ [40] gives the ratio $\tau_d/\tau_s = 9.7$. The value of τ_s calculated by formula (3) at $T = 298$ K ($a = 0.0957$ nm (the H bond length) [41] and $\eta = 0.89 \times 10^{-3}$ Pa s [28]) is $\tau_s = 2.4$ ps. Despite the fact that τ_s differs from the experimental value, the above data indicate that it is possible to use the Debye formulas to estimate the order of magnitude of the water relaxation times.

As shown earlier, at the bubble compression stage, a high-pressure zone, up to about 3−6 GPa, is formed in water near the interface. Water viscosity at increased pressures has been determined using different methods. However, the data obtained are scarce and contradictory. Thus, in [42], the same viscosity was obtained using the Walden law as under normal conditions: $\eta = 10^{-3}$ Pa s ($P_w = 7$ GPa). In [43], the viscosity at $P_w = 31$ GPa is about the same for some metals and water $\eta \simeq 10^3$ Pa s. Apparently, the most direct method for determining η by the acceleration of a cylindrical conductor in the medium behind the SW front is used in [44]. Here $\eta = 2$ Pa s is obtained at $P_w = 6.5$ GPa. In [45], the authors determined the viscosity by the width of the SW front and obtained $\eta = 20$ Pa s at $P_w = 10$ GPa. Using this viscosity value made it possible to describe the experimental time dependence of the shock polarization [45].

Taking into account that the above-considered methods for determining η are mainly indirect, we estimate its value in the pressure interval 3−6 GPa,

which is of interest to us, as follows. We assume the value $\eta = 2$ Pa s ($P_w = 6.5$ GPa) determined by the most direct method to be the reference value [44]. Further, assuming that the viscosity is a linear function of pressure, we get a rough estimate for η: $\eta = 0.9$ Pa s ($P = 3$ GPa) and $\eta = 1.8$ Pa s ($P = 6$ GPa).

By calculating the relaxation times at room temperature considering these values, provided the dielectric permeability is independent of pressure, using formulas (2) and (3), we obtain:

$-\tau_s = 2.4$ ns, $\tau_d = 23$ ns at $P = 3$ GPa and

$-\tau_s = 4.8$ ns, $\tau_d = 46$ ns at $P = 6$ GPa.

According to [1], the bubble wall velocity at the final stage of the collapse reaches the values of 1000–1500 m/s^{-1}. To estimate the distance between the spherical capacitor plates by formula (1), we assume that the bubble wall velocity $\overline{V} = 10^3$ m/s. Then, considering the calculated τ_d, we obtain $L_p = 23$ μm ($P = 3$ GPa) and $L_p = 46$ μm ($P = 6$ GPa).

We estimate the electric field strength in water for the experiment under consideration: $p_0 = 1$ atm, $p_a = 1.3$ atm, $f_a = 26$ kHz, $R_0 = 5$ μm. To determine the field formed due to the DEL evolution, we use the Ostrogradsky–Gauss theorem.:

$$E_{DEL} = \frac{eNs_{min}}{\varepsilon\varepsilon_0}\frac{R_c^2}{r^2}, \quad r \geq R_c, \quad (4)$$

where ε_0 is the electric constant; e is the electron charge; and Ns_{min} is the surface density of dipoles.

Given the previously determined value $Ns_{min} \approx 10^{15}$ cm^{-2} we obtain $E_{DEL} \simeq 10^9$ V/m ($r = R_c$) and $E_{DEL} \simeq 10^8$ V/m ($r = 3R_c$).

2.2. Flexoelectric Effect

The flexoelectric effect (FE) is defined as an electric response of a dielectric condensed medium (polarization) to the action of a deformation gradient [16]. In the one-dimensional case [16],

$$P_f = \gamma\nabla\varepsilon_{el} = \gamma\beta\nabla p. \quad (5)$$

where P_f is the polarization; ε_{el} is the elastic deformation; γ is the flexoelectric coefficient; β is the medium compressibility; and p is the pressure.

The FE is inherent in all dielectrics and describes the polarization occurrence in a non-piezoelectric medium under mechanical action. When describing the flexoelectric effect, the following expression derived from (5) is also used for the electric field strength E_f:

$$E_f = \frac{\gamma\beta}{\varepsilon\varepsilon_0}\nabla p \equiv f\nabla p, \quad (6)$$

For solids, the FE has been investigated both theoretically and experimentally. The results of theoretical research were most fully described in [16]. It was shown that the flexoelectric coefficient had an order of magnitude e/a (e is the electron charge, a is the lattice constant) $\sim 10^{-9}$ C m^{-1}. Note that in [16], only ion crystals were considered. The experiments were carried out mainly with ferroelectric materials in the nonpolar (paraelectric) phase [46–50]. It was shown that the flexoelectric polarization was a linear function of the deformation gradient up to its values 0.015–0.020 m^{-1}; the order of magnitude of the flexoelectric coefficient γ ranged from 10^{-8} to 10^{-9} C/m (strontium titanate single crystal) [50], or up to 10^{-4} C/m (barium strontium titanate ceramics) [48]. Data on studies of the FE in liquid dielectrics are almost non-existent. We are aware only about the theoretical estimations of the order of magnitude of the coefficient f for water presented in [11, 12]. The authors considered two possible dielectric polarization mechanisms: charge shift and dipole ordering (orientation polarization). The estimate of f at the first type of polarization was performed using ion crystals as the model substance. The consideration of the second type of polarization is based on the statement that the orientation polarization is much more efficient than the sift polarization, because the dielectric constant of polar dielectrics is much larger than that of nonpolar dielectrics. Finally, we obtain the following:

$$f \sim 10^{-7} \text{ V/Pa}, \quad \gamma \sim 10^{-7} \text{ C/m}.$$

In our opinion, the method proposed in [11, 12] is only suitable for a very rough estimation of f and γ, because some factors are not taken into account, which can lead to large errors when it is used to calculate electric fields. Note, in particular, that in [11, 12], the influence of the thermal motion of molecules was not considered when determining polarization.

In [51], an approach to the evaluation of FE coefficients was proposed based on studying the polarization of dielectrics by the electric field and the polarization of condensed dielectric medium in an inhomogeneous field of the shock wave front forces (shock polarization). Analytical expressions for the orientation polarization and the coefficient of flexoelectric effect were obtained with consideration of temperature. In particular, the FE coefficient $\gamma = 3.7 \times 10^{-12}$ C m^{-1} for water at normal temperature, which is five orders of magnitude lower than the value obtained in [11, 12], and two to three orders of magnitude lower than the theoretical estimates for the solid [16]. The tests of the approach [51] using the results of experiments on measuring shock polarization in water and nitrobenzene showed that it could be used to assess the polarization of liquids in heterogeneous pressure fields.

When estimating the field strength resulting from the flexoelectric effect (formula (6)) the value $E_{fe} \simeq 10^5$ V/m was obtained at $\nabla p = 10^{17}$ Pa/m. The coefficient f was determined from the value $\gamma = 3.7 \times$

10^{-12} C/m [51] and water compressibility $\beta = 4.5 \times 10^{-10}$ Pa^{-1} [28]. The obtained value E_{fe} is 4 orders of magnitude smaller than E_{DEL}.

2.3. Thermoelectric Effect

The thermoelectric effect (TE) is the emergence of an electric field in the polar liquid when there is a temperature gradient in it. The TE equation [17, 18] can be written as follows:

$$\mathbf{E}_{\mathrm{TE}} = g \nabla T, \qquad (7)$$

where g is the thermoelectric coefficient.

TE was theoretically predicted in [17] devoted to the simulation of heat transfer in water by the nonequilibrium molecular dynamics method.

In [18], the author considered the TE at the molecular level based on the following assumptions.

Due to the temperature gradient, a polar nonsymmetric molecule acquires a difference in the values of free energy at different orientations relative to the gradient. Therefore, the molecules acquire a dedicated direction of orientation in a heterogeneous temperature field.

Using the molecule model in the form of a rigid dumbbell (rigid rotator) and applying the averaging of the dumbbell orientation over the Boltzmann factor, the author of [18] obtained an analytical expression for the thermoelectric coefficient. It was shown that g was a function of temperature and geometrical parameters of a molecule of liquid. Note that the consideration of TE in [18] is similar to the consideration of FE in [51].

The estimation of the thermoelectric coefficient for water in water–Ar and water–N$_2$ systems at the thermodynamic parameters obtained in the present work gave the following values: $g_{\mathrm{Ar}} = -0.02$ V/K, $g = -0.03$ V/K. Using the temperature gradient value $\nabla T \approx 10^{11}$ K/m, we obtain $E_{\mathrm{TE}}^{\mathrm{Ar}} = 2 \times 10^9$ V/m, $E_{\mathrm{TE}}^{\mathrm{N_2}} = 3 \times 10^9$ V/m. Since $g < 0$, the field strength vector is directed from gas to liquid.

In [52], g was calculated using the method of nonequilibrium molecular dynamics. The TIP4P/2005 water model was used. It was shown that within this model, the thermoelectric coefficient strongly depended on the thermodynamic state and varied in the range from $+10^{-4}$ V/K at temperatures close to normal to -10^{-2} V/K at temperatures close to critical conditions; here, $g \approx 0$ in the temperature range 400–650 K. The evaluation of the field strength for the water–nitrogen system ($T_{\mathrm{w}} = 800$ K, $g \approx -10^{-3}$ V/K [52]) gave the value $|E| = 10^8$ V/m. The field was directed from gas to liquid. In [52], there were no calculations of the thermoelectric coefficient for higher temperatures (water–argon system).

Thus, three effects are considered, due to which an electric field may emerge in water near the bubble wall at the last stage of the bubble compression. With the same initial conditions, a field with maximum characteristics is formed due to the double electric layer evolution: electric strength of up to 10^9 V/m and the radial dimensions of the field region of few tens of micrometers. The field strength vector is directed to the center of the bubble. The field that emerges due to the flexoelectric effect has the same direction, but its strength does not exceed 10^5 V/m. The estimated strength of the field formed by the thermoelectric effect is 10^8–10^9 V/m. The strength vector is directed from gas to liquid. The dimension of the region where the field arises due to FE is 1–2 µm, and for the field that emerges due to TE, it is 2×10^{-8} m.

The effects considered should also occur in other polar liquids. In nonpolar liquids, the electric field can only occur due to the flexoelectric effect and only due to the charge shift in molecules in the pressure gradient field. However, here, the field strength cannot exceed $E \sim 10^5$ V/m obtained for water, because in the latter case, the orientation polarization is also considered.

3. SOURCES OF EMISSION IN POLAR AND NONPOLAR LIQUIDS

As stated above, the polarization model is based on the assumption that there are two sources of emission: thermal and electrical [13, 14]. The first source of emission is an adiabatically heated gas inside a bubble when it collapses; the second one is an electric breakdown channel in liquid. It can be assumed that the thermal source of emission is the main and most likely the only source in the case of nonpolar liquids. In systems with polar liquids, both sources of emission do work. The thermal source of emission has been quite well studied theoretically. Scenarios of high temperature zone formation with variations of considering heat conductivity, diffusion, evaporation, condensation, etc. are presented in many papers, e.g. in [1, 3, 23, 24]. Within the proposed models, the zone dimension is equal to the minimum radius of the bubble, the state of the substance inside which is characterized by the temperature of $\sim 10^4$ K and density of 1 g cm^{-3}. The mechanism of emission is a recombination of electrons and ions and bremsstrahlung when electrons are scattered by neutral atoms and ions, while the recombination and bremsstrahlung from neutral atoms makes the major contribution [23, 24, 54].

The final thermodynamic state of the substance at bubble collapse depends on the liquid–gas system composition, initial conditions, and parameters of the acoustic impact. The fact that plasma can form in a bubble is shown both experimentally [57–59] and theoretically [19, 20, 23, 24, 54]. In [57–59], the degree of argon ionization and the concentration of free elec-

trons were determined when studying the H_3PO_4 (85 wt %)-Ar system. The latter was $10^{17}-10^{21}$ cm^{-3} at $p_a = 2.7-3.8$ bar.

Compare the results of the calculations (Table 1) with the experimental results.

A bubble with the equilibrium radius $R_0 = 5$ μm contains $\sim 10^{10}$ nitrogen and argon atoms. According to the calculated value of the ionization degree, the number of free electrons in N_2 and its mixtures with Ar ($\alpha_G \sim 10^{-10}$) is nonsignificant. Consequently, according to the hypothesis [23, 24], SL should not be observed when using these gases, but should occur when using Ar ($\alpha_G \sim 10^{-2}$).

In experiments [1, 3] carried out under the initial conditions and with the parameters of influence close to the calculated ones, water was used with the following gases: atmospheric air, pure N_2, pure O_2, and their 80/20 mixture. The experimental results: SL was unstable for pure gases; the light output was $\sim 0.02-0.03$ for N_2, and it was $0.03-0.04$ for O_2, in comparison with air, for which a bright stable SBSL was observed. The addition of noble gases to nitrogen and oxygen resulted in the SBSL stability and increased the light output. He, Ar, and Xe were added to N_2. The dependence of the light output on their concentration was qualitatively the same: growth with the increase in concentration up to 1% (maximum 0.6 (He), 1.0 (Ar) and 1.1 (Xe) in relation to air). Further, as the concentration increased, there was a slow decline to 0.3 (He, Ar) and 1.2 (Xe) at 100%. The same qualitative picture was observed for oxygen and its mixture with nitrogen. In [60, 61], a stable SBSL was obtained in the water−N_2 system at lower temperature ($\sim 7-9$°C) in the acoustic pressure range of $1.3-1.4$ atm. Here, the luminous intensity was ~ 1% in relation to air. The emission spectrum was described by a smooth curve, spectral density increased with the decrease in wavelengths. The described results contradict the calculations: the addition of 1% of Ar to nitrogen practically does not increase the degree of the gas ionization, and the calculation of α_G of nitrogen at the initial temperature of 9°C gives three times lower value than at normal temperature [22].

The argon rectification hypothesis was put forward to explain the experiments with the water−air system [62]. According to the hypothesis, the pressure and temperature inside the bubble at collapse are sufficient to dissociate molecular nitrogen, oxygen, and water. The resulting radicals react with each other to form water-soluble compounds (NO, HNO_2, etc.), which are removed from the bubble due to diffusion. As a result, only argon remains in the bubble, which plays the major role in the light emission. Based on the rectification hypothesis, it was concluded that the presence of inert gases is necessary to obtain a stable SL.

However, such experimental facts as the observation of a bright stable SBSL in experiments with the

Table 2. Features of electron motion in water

E, V/m	l_e, nm $I = 12.6$ eV	l_e, nm $I = 6.5$ eV	t_e, s $I = 12.6$ eV, $I = 6.5$ eV
10^9	7.8	3.9	$\sim 10^{-14}$
10^8	78	39	$\sim 10^{-13}$
10^7	780	390	$\sim 10^{-12}$

inert gas mixtures with N_2, and especially with O_2, as well as the registration of maximum light output in these systems at 1% concentration of Ar, in addition to the experiments with air, cast doubt on the value of the rectification hypothesis and, thus, on the possibility to explain the results of the experiments using only one thermal source of emission. Another argument here is the stable SBSL in the water−N_2 system [60, 61].

Thus, the examination indicates serious difficulties in describing the results of experiments using a single thermal source of emission.

The electric field that has emerged in liquid at a bubble collapse with the strength vector directed towards the bubble center creates grounds for electron acceleration in the direction away from the center. When the energy reaches the value of the ionization potential of molecules of liquid, the conditions for an electron avalanche due to the impact ionization are created. In Table 2, there are estimates of the length of electron paths l_e, after which the electron energy equals the potential of water ionization ($I = 12.6$ eV for steam [28] and $I = 6.5$ eV for liquid considered as an amorphous semiconductor [63, 64]), and the times t_e, which should be spent for this purpose under the condition of uniformly accelerated motion. The known expression is used for the estimation:

$$l_e = \frac{I}{eE}, \tag{8}$$

where I is the ionization potential.

Based on the data in Table 2, it can be assumed that the electron avalanche can be formed when the dimensions of the field region are $L_p \simeq 1$ μm, because in this case, at the strength $E \geq 10^8$ V/m, the condition $L_p \gg L_e$ is met. Therefore, the development of an electric breakdown in the liquid by an avalanche mechanism is also possible. These processes must be accompanied by luminescence due to recombination, bremsstrahlung, and electron transitions in excited atoms and molecules; therefore, the breakdown channels can be considered as the second source of emission.

Breakdowns are impossible in nonpolar liquids ($E \leq 10^5$ V/m).

4. ELECTRON SOURCES

Free electrons are needed to make the considered hypothetical sources of emission work. One of possible electron sources is certainly plasma, which is formed by the collapse of a bubble due to thermal ionization of gas (steam–gas mixture). Free electrons can enter the region of electric field in liquid and cause breakdowns.

Liquid may be the second source of electrons, as shown in [12] when considering the water–argon system. According to the literature [63, 64], the authors [12] considered water as an amorphous semiconductor with the energy gap width of 6.5 eV (ionization potential), whose electronic conductivity grew with the increase in temperature. In [12], it was estimated that at the final stage of collapse, which duration was ~1 ns, a thin layer of water was heated to a high temperature due to high temperature of gas. This should lead to free electron generation in the layer due to the thermal ionization.

In [12], the authors took only the temperature into account. It is known that the electron–atom bond can be weakened and broken by temperature and some other factors, including the impact of pressure and strong electric field that occur when the bubble collapses. Note also that water and other polar liquids may be ordered structures near the water–gas interface due to creation of DEL and manifestation of FE, which may affect their semiconductor properties. In the papers that considered water as an amorphous semiconductor, this factor was not taken into account.

We estimate the efficiency of water as an electron emitter. Following [63, 64], we consider water to be an amorphous semiconductor with the energy gap width $E_{go} = 6.5$–6.9 eV under normal conditions. We assume that at the final stage of collapse, there are the following influences on the water near the interface:

—high pressure $P_w = 3$–6 GPa [20];

—high temperature (heating by gas); and

—strong electric field up to 10^9 V/m.

Data presented in the literature show that the increase in pressure and temperature leads to changes in the energy gap width E_g. According to [28], for solid semiconductors with the energy gap width $E_{g0} \leq 3$ eV, under normal conditions, the pressure increase can result in either negative (silicon) or positive (germanium) increase in this value. When the temperature rises, the increase in E_g is always negative.

Assume that the combined effect of pressure and temperature results in a significant decrease in E_{g0}. We estimate the free electron density in water due to ionization by an electric field and thermal ionization at two values of E_g: $E_g = E_{g0} = 6.7$ eV and $E_g = 4$ eV. For the first estimation, we use the Zener formula for the probability of ionizing solid dielectrics by the field

obtained by using the mechanism of quantum mechanical electron tunneling [65].

$$W_E \cong \frac{eEd}{h} \exp(-\beta), \qquad (9)$$

where e is the electron charge; E is the electric field strength, d is the lattice constant; and h is the Planck constant.

Formula (9) is obtained under the following condition:

$$\beta = \frac{\pi^2 m_{ef} d E_{go}^2}{e h^2 E} \gg 1.$$

Here m_{ef} is the electron effective mass.

The concentration of free electrons is estimated by the formula:

$$n_{eE} = W_E n_{val} \tau, \qquad (10)$$

where n_{val} is the valence electron concentration and τ is the duration of the final stage of the bubble compression.

Calculation by (9) and (10) showed that at $E_g = 6.7$ eV, the density of free electrons is $n_{eT} \sim 10^{21}$ m^{-3} at $E = 5 \times 10^8$ V/m, and $n_{eT} \sim 10^{28}$ m^{-3} at $E = 10^9$ V/m. The dimensions of the water ball layer (the field region) are assumed equal to $R_{min} = 0.5$ μm and $R_{max} = 1.5$ μm. The layer volume $V = 1.3 \times 10^{-17}$ m^{-3}. Hence, at $E = 5 \times 10^8$ V/m, there are ~10^4 electrons generated, and at $E \sim 10^9$ V/m, there are 10^{10} electrons generated. At $E_g = 4$ eV, the amounts are much larger. For the calculations, we assume that $m_{ef} = m_e$, $\tau = 1$ ns, and n_{val} is the concentration of water molecules.

According to the calculations (Table 1) and experiments [1–5], the gas temperature at bubble compression can reach significant values. At the final stage of the collapse, which duration is ~1 ns, the liquid layer can be heated by gas to the temperature of thermal ionization. The concentration of free electrons in this process is described by the formula [66]:

$$n_{eT} = 2\left[\frac{m_{ef} KT}{2\pi h^2}\right]^{3/2} \exp\left(\frac{\mu - E_g}{KT}\right), \qquad (11)$$

where μ is the chemical potential and T is the liquid temperature.

By substituting into (11) the expression for chemical potential in the form of [66] $\mu = \frac{1}{2}E_g + \frac{3}{4}T \ln\frac{m_{ef}}{m_e}$, we obtain the following formula to estimate n_{eT}:

$$n_{eT} = 2\left[\frac{m_{ef} KT}{2\pi h^2}\right]^{3/2} \exp\left(-\frac{E_g}{2KT}\right). \qquad (12)$$

Here we assume $m_{ef} = m_e$.

The calculation by formula (12) for water with $E_g = 6.7$ eV gives the following values: $n_{eT} = 1.7 \times 10^{25}$ m^{-3}

for the water–argon system and $n_{eT} = 5.4 \times 10^{19}$ m^{-3} for the water–nitrogen system. The water temperature was previously determined from the calculated temperature of gas (Ar, N$_2$) presented in Table 1.

5. POLARIZATION MODEL TESTING PROPOSAL

The estimations performed showed that an electric field of high strength can be formed in water near the liquid–gas interface of a collapsing bubble, and free electrons can appear. The same effects can be expected to take place in other polar liquids. These circumstances create conditions for electrical breakdowns, which is a significant argument in favor of the polarization model.

Note, however, that insufficient study of the double electric layer in liquid–gas systems, lack of experimental data on flexoelectric and thermoelectric effects in water, the inconsistency of experimental results on measuring the pressure dependence of water viscosity, and consideration of water as an amorphous semiconductor do not give enough grounds to consider the estimations sufficiently accurate. These estimates can be considered as majorant, but the results obtained for SL by using these estimates should be tested experimentally.

In our opinion, the most reliable and efficient way to prove the existence of an electrical source of emission may be an experiment on registration of electromagnetic radiation emitted in the radio range during an electrical breakdown. Such experiments on studying hydrodynamic luminescence were successfully accomplished and presented in [67]: electromagnetic radio interference pulses synchronous with light pulses were recorded.

CONCLUSIONS

In [13, 14], a polarization model of sonoluminescence was proposed based on the assumption of existence of two emission sources: thermal and electric. The first source was adiabatically heated gas inside a bubble, and the second one was breakdown channels in liquid. The electric source occurs only in polar liquids.

In the present work, concerning the development of ideas about the electric source, the electric field strength in water near the liquid–gas interface of a collapsing bubble is estimated. A double electric layer and flexo- and thermoelectric effects are considered as field sources. It is shown that the field strength can reach 10^9 V/m, while the dimensions of the strong field region are few micrometers. Free electrons in water can originate from plasma generated inside the bubble; they can also emerge due to water ionization by the electric field and water thermionization. The presence of a strong field and free electrons make possible the development of electrical breakdowns in liquids by the avalanche mechanism; the channels of this process can be considered as the second source of emission. The breakdown should be accompanied by electromagnetic emission in the radio range, whose registration can be used to test the proposed model.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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