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CONTEMPORARY VIEWPOINT ON NATURE OF MULTIBUBBLE SONOLUMINESCENCE

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The problem of uncompensated charge arising on the surface of a deformed cavitation bubble is solved in general view. The maximum electric strength is accounted. In the terms of the electric theory of local electrification of cavitation bubbles the explanation of some physical and physico-chemical effects in the cavitation fields is proposed. The theory of local electrification is shown to be now the single one, which correlates with a majority of experimental data on multibubble cavitation fields. Experiments of Lauterborn with laser cavitation, that have shown that at bubble deformation the luminescent glow registered near the bubble surface and the light-emitting spot was localized at the point of maximum curvature, but not in the center of the bubble, are analyzed. This result is a direct experimental evidence of the theory of local electrification and, particularly, the model of electrification of the surface of deformed cavitation bubble when the deformation is approximated by a paraboloid of rotation. A criterion of influence of bubble surface deformation on extreme parameters at bubble collapse in multibubble cavitation fields is proposed.

Knowledge of the mechanism of the sonoluminescence (SL) and sonochemical reactions initiation gives the possibility to intensify these processes and direct them in the necessary way. Now for explanation of these processes usually one apply the heat or electric theories. Because of unsatisfactory of the heat theory and also earlier electric theories, electric theory of the local electrification of the cavitation bubble is very important for understanding SL and sonochemical reactions [1,2].

Electric phenomena in the cavitation fields are a result of the electric double layer formation on the surface of cavitation bubbles. Let x the distance from the liquid surface to the point considered. Accordingly to the Stern – Helmholtz scheme, this layer consists of dense layer having thickness d_0 (electric potential is changed linearly from the thermodynamic potential \mathbf{y}_0 to some potential \mathbf{j}_d), and diffusive one (dependence of potential is exponential), which balances the charge of dense layer. At $x > x_s$ (where x_s is a co-ordinate of the slide boundary and its potential is equal to electrokinetic \mathbf{z} -potential) acoustic flows wash out the part of diffusive layer, so the uncompensated charge on the bubble surface arises. The surface density of the charge is determined by

where ϵ is the dielectric capacitivity of liquid, ϵ_0 is the dielectric constant. For water $d_0 \approx 1$ nm and d_0

$$\mathbf{s}_{el} = \frac{\epsilon\epsilon_0(\mathbf{j}_d - \mathbf{z}) \cdot \ln(\mathbf{j}_d / \mathbf{z})}{x_s}, \quad (1)$$

$\ll x_{\bar{n}} < 100$ nm, $\mathbf{z} \approx 0.05 \text{ \AA}$. We should note that \mathbf{s}_{el} doesn't depend on the bubble surface curvature as the curvature radius $\gg x_s$ as well as on the bubble wall velocity if the velocity is moderate. Analysis of the electric phenomena requires the consideration not the spherical cavitation bubbles (electric field inside these bubbles is zero) but deformed bubbles. Deformations of bubble surfaces in a liquid occur very often at the different experimental conditions: in acoustic waves, during vibrations, in hydrodynamic flows, by action of lasers, by explosion of tungsten filaments etc. Deformations of cavitation bubbles in acoustic fields can appear at very low amplitudes of sound pressure ($\sim 10^{-2}$ atm).

1. Electric field on surface of fragmented cavitation bubble.

Splitting of cavitation bubbles leads to splinter bubble separation. The balance of uncompensated charge on the bubble neck is determined by equation $dQ = (I - i)dt$, where I and i are currents of charging and discharging because of liquid conductivity [3],

$$I = \mathbf{p}\epsilon\epsilon_0\mathbf{z} \frac{r_\sigma^2}{lm} \Delta p, \quad i \leq \frac{Q}{2\epsilon\epsilon_0 I_0} \cdot \frac{r_\sigma}{x_c}, \quad (2)$$

where m and I_0 are viscosity and specific electrical resistivity of liquid, r_σ and l are the radius and the length of the neck at the moment of fragmentation. Acoustic field must overcome the pressure drop for

bubble fragmentation, and

$$\Delta p = \frac{\mathbf{s}}{r_n} + \frac{16}{3} \mathbf{p}^2 f^2 a r \frac{r^3}{r_n^2} + 12 \mathbf{p} m a f \frac{r}{r_n^2} + \frac{Q^2}{8 \mathbf{p}^2 \mathbf{e} \mathbf{e}_0 r_n^2 l^2}$$

where \mathbf{m} and \mathbf{l}_0 are surface tension and density of liquid, r_n and l are amplitude and frequency of acoustic field, r is bubble radius. A cavitation bubble in acoustic field overcomes the force of the surface tension, of the bubble perturbation, the Stokes force and electrostatic forces of push off between the same charges on the wall of the collapsing neck of the fragment bubble. These effects make difficulties to fragmentation of the cavitation bubble, and the energy for overcoming them accumulates, the part of it can be transformed into the energy of electric charges separation and local electrification of the neck surface and then into the energy of electric discharge. Assuming that parameters of acoustic field do not change at fast bubble splitting, we obtain [4]

The charge on the surface of splitting bubble neck at the moment of disintegration is sorbed on a small

$$Q \approx \frac{\mathbf{p} \mathbf{e}^2 \mathbf{e}_0^2 \mathbf{l}_0 \mathbf{z} x_c}{m r_n} \left(\mathbf{s} \cdot r_n + \frac{16}{3} \mathbf{p}^2 f^2 a r r^3 + 12 \mathbf{p} m a f r \right) \cdot \exp \left(\frac{-1}{4 \mathbf{e} \mathbf{e}_0 \mathbf{l}_0} \frac{r_n}{x_c} t \right) \quad (3)$$

region having radius $\sim r_n$ and it is divided in two. Electric strength near the region of neck splitting is $E_{max} = Q(0)/(2 \mathbf{p} \mathbf{e}_0 r_n^2)$ [3]. For usual parameters of cavitation bubble at $r_n = l = 10^{-6}$ m, $x_c = 10^{-7}$ m, $a = 10^{-5}$ m, $f = 20$ kHz in water ($\mathbf{r} = 10^3$ kg.m $^{-3}$, $\mathbf{m} = 10^{-2}$ poise, $\mathbf{e} = 81$, $\mathbf{z} = 0.05$ V, $\mathbf{s} = 73$ mH.m, $\mathbf{l}_0 = 10^3$ Om.m) we obtain $Q(0) = 8,5 \cdot 10^{-14}$ Cl. Local density of uncompensated charge per $\mathbf{p} r_n^2$ is $\langle \mathbf{s}_{el}(0) \rangle = 2,8 \cdot 10^{-2}$ Cl.m $^{-2}$. So, the electric strength $E_{max} = 1,5 \cdot 10^9$ V.m $^{-1}$ occurs much more than the critical one at standard conditions $E_{cr1atm} = 3 \cdot 10^6$ V.m $^{-1}$, and probability of electric discharge is great. The character time of discharging because of electroconductivity is much smaller than $f^{-1} \sim 5 \cdot 10^{-5}$ s but it is much more than splitting time.

We can estimate the duration of electric discharge by using of equation of electron movement under action of constant electric force ($-e E_{cr}$). We will also take into account velocity changing from 0 to $e E_{cr} t / m_e$ on free path, where m_e – is electron mass and t is time between two collisions of electron. Then rupture time is determined by [5]

$$t_{i\partial} \sim 10t \approx 10 \cdot \sqrt{\frac{2m_e l}{e E_{cr}}} \quad (4)$$

At $l = 10^{-7}$ m and $E_{cr} = 3 \cdot 10^6$ V.m $^{-1}$ we obtain: $t_{i\partial} \sim 10^{-11}$ s. Accordingly to (4), Q and its relaxation time decrease at decreasing of specific electrical resistivity of liquid. But **characteristic time of electric rupture occurs much smaller than relaxation time of the charge due to electroconductivity** even at small liquid resistivity. So Q can relax due to electroconductivity only if discharge does not happen for some reason.

2. Electric fields on surface of deformed cavitation bubbles.

We have shown that for the total solution of the problem of the electrification of the surface of the cavitation bubbles during pulsations and deformation it is necessary to consider in general view two types of deformation: radial and annular. In our work [6] we have considered the electric field inside a neck between the main and the splinter fragments of the bubble or, as a limit, at arising of the annular streams. We approximated the neck as **one cavity hyperboloid of rotation** around the axe of symmetry. We have demonstrated that in this case high electric strength arises also, and at some conditions (especially in the presence of the ring cumulative jets) electric discharge can take place. Nevertheless, electric strength occurs much smaller than in the case of bubble splitting.

At bubble surface deformation, that arise under the action of the radial forces (radial jets for example), it can be approximated by a **paraboloid of rotation** having the depth H and the root radius r_p [7]. In the process of the cumulative stream formation maximum of electric strength corresponds to the point of the highest curvature - at the end of paraboloid. At $H/r_p > 2$ it is described with a great accuracy by the sum ($E_p + E_s$) of electric strengths from the paraboloid E_p and from the spherical part of deformed cavitation bubble E_s , correspondingly,

$$E_p \approx \frac{n \cdot S_{el}}{e_0} \cdot \int_0^b \frac{\sqrt{1/4 + t^2}}{(1 + t^2)^{3/2}} dt \equiv \frac{n \cdot S_{el}}{e_0} \cdot I(b), \quad E_s \approx \frac{S_{el}}{e_0} \cdot \frac{r^2}{(r + H)^2}, \quad (5)$$

where integral I is a function of b and $b \propto H/r_p$. If $b < 2$ then $I \gg b/2$, if $b > 5$ then $I \approx 1,1$ and $n(H/r_p)$ is the coefficient of electric strength increase because of surface curvature, $n \propto I$. For example, if $e = 81$, $y_d = 0,08$ V, $z = 0,055$ V, $x_s = 10^{-7}$ m and $b > 5$ we obtain: $E \gg 1,5 \cdot 10^7$ V.m⁻¹, $E > E_{cr1atm} = 3 \cdot 10^6$ V.m⁻¹. A rupture in the deformed cavitation bubble can arise by execution of an additional condition: $H > 5I_0$ (I_0 is the free length of electron). For normal conditions in air ($t = 20$ °C, $p = 10^5$ Pa): $5I_0 = 4 \cdot 10^{-7}$ m $< H$. So discharge can arise even at pressure 1 atm in a bubble let alone smaller pressure [7].

3. General analysis of theoretical and experimental results on multibubble cavitation.

We believe that only two theories explaining the mechanism of multibubble SL are most developed and valid today: the heat theory and the theory of local electrification of the cavitation bubbles. Development of heat or electric nature of multibubble SL in multibubble fields is one of the fundamental problems of sonochemistry. Conformance of the basis experimental data to these theories is presented in Table 1 [2,8].

Table 1. Correlation of experimental results to the heat theory and the theory of local electrification of cavitation bubbles⁴ for multibubble cavitation.

	Experimental results	Heat theory	Theory of local electrific
1	Maximum of probability of sonoflashes when $r \sim 0,8 R_{max}$	-	+
2	SL and sonochemical reactions at $f \sim 100$ Hz; absence of collapse of cavitation bubbles ($R_{max} \sim 1$ cm)	-	+
3	Spectra of SL considerable differs from the black body spectra ^{**}	-	+
4	Non symmetric form of sonoflashes	-	+
5	Intensity of SL of D-line of Na decreases strongly when the space between pulses increases	-	+
6	SL at $T_\infty \sim T_{boil}$ (and p_h is about p_v)	-	+
7	Increasing of SL on constant electric field or on electrolysis	±	+
8	SL at the fast evacuation	-	+
9	Presence of electric pulses in cavitation field	±	+
10	Light emission in Hg and in melts of metals	-	±
11	SL in liquids with great viscosity and in polymers when their melting begins	-	+
12	SL and sonochemical reactions at very low intensity of sound ($\sim 10^{-3}$ W.cm ⁻²)	-	+
13	Absence of H ₂ O ₂ and synthesis of NO at the work of devices of pulse adiabatic compression; synthesis of H ₂ O ₂ at electric discharges in water	-	+
14	Random time of sonoflashes emission	-	+
15	SL quenching; the linear dependence of efficiency of quenching U/U^Q on the concentration of admixture	-	+
16	Dependence of U/U^Q on the structure of quencher; increasing of U/U^Q when the T_{boil} of quencher grows	-	+
17	Increasing the T_{boil} of quencher leads to increasing of the inhibition efficiency of the sonochemical reactions	-	+
18	SL is cold luminescent glow (on the basis of 15-17)	-	+
19	Experiments with deformed laser bubble: light emission from the region near the surface at the point of maximum curvature, but not from the bubble center	-	+

⁴ Symbol + denotes consistency with theory, - denotes lack of consistency, ± denotes that difficulties appear in making theory agree with experimental results.

** By using of chemiluminescent mechanism (it is a modification of the heat theory) proposed by Griffing [9], one can explain this difference. But this theory can not explain other points in this table.

In the frame of heat theory it is difficult to explain the initiation of multibubble SL and sonochemical reactions at the low intensity of sound ($\sim 10^{-3} \text{ W.cm}^{-2}$) and at high viscosity of liquid. The collapse of the cavitation bubble when T_∞ is about T_{boil} or at low static pressure, when $p_h \sim p_s$ (p_s – saturated vapor pressure), is impossible because process of bubble growing becomes much more probable. At very small intensity of sound and high viscosity of liquid the amplitude of bubble pulsation is so small that the collapse of bubble is impossible even theoretically. Accordingly to equations of cavitation bubble dynamics, if the heat mechanism took place, the form of SL flashes would be symmetric. This conclusion is confirmed by experimental data on single bubble SL [10,11] (at single bubble collapse high temperature is apparently reached). But at multibubble SL rapid rising and slow dropping take place as well as luminescent glow at usual electric discharge.

We should note that existence of even one experimental fact contradicted to the heat theories does them noncompetitive in comparison with the electrical ones, and followers of the heat theories must disprove all experimental data considered in Table 1.

The crucial experiment in favour of electric theories seems to be the one of Lauterborn et al [12,13]. They the first could directly register the localization of light emission region at collapse of laser cavitation bubble. At spherically symmetric bubble collapse of laser bubble, SL is emitted from rather small region of radius $\sim 0,1 r_{\text{min}}$ (minimum bubble radii $r_{\text{min}} \sim 10\text{-}15 \text{ mkm}$) inside the bubble center. Presence of solid surface or another cavitation bubble brings to arising of high-speed radial cumulative jets directed toward to the solid surface or to the other bubble. In this case the energy of emitted light strongly depends on parameter $\gamma \equiv l/R_m$, which characterises unspherisity of bubble compression (l is the distance from the bubble center to the solid surface and R_m is the maximum radius of the bubble). Even if $\gamma = 9$, the SL intensity is only a half of that at spherical bubble collapse, if γ decreases from 9 to 4, intensity decreases rapidly, and at $\gamma < 3.7$ the glow is absent at all (in the limits of used apparatus perceptibility). At $\gamma = 4.7$ unsymmetric collapse of the laser bubble was observed. At the stage of symmetric collapse SL wasn't registered. Nevertheless at deformation the luminescent glow was detected **near the bubble surface and the light-emitting spot was localized at the point of maximum curvature, but not in the center of the bubble (distance from bubble center to light emission point is about 135 mkm)** (Fig.2). We consider this result as a **direct experimental evidence of the theory of local electrification** [2], proposed by us and, particularly, of the model of local electrification of the surface of deformed cavitation bubble when the deformation could be approximated by a paraboloid of rotation [7]. Besides, high temperature inside deformed bubble during compression is not reached because SL at this stage is absent.

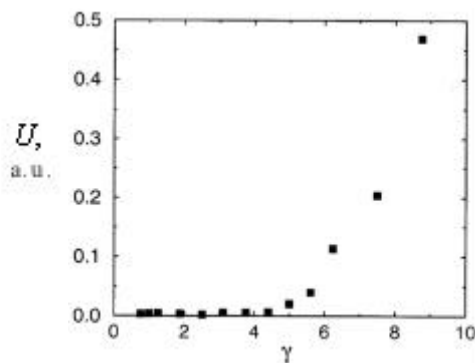


Figure 1. Luminescence of an asymmetrically collapsing laser-generated bubble. Dependence of light intensity (a.u.) on the distance parameter γ .



Figure 2. Localisation of a glow region near the deformation of bubble surface in the point of maximum curvature but not in the bubble center (at unsymmetric collapse of a laser-generated bubble).

We can propose some criticisms about assumptions of a few authors that SL may be a result of a strong hit of radial cumulative jet into an inner bubble wall:

- At SL regime this strong hit is absent because if it took place than another cumulative jet having opposite direction (contrjet) would arise. But absence of contrajet at SL regime is registered experimentally;
- a contrjet (and therefore a strong hit) arises at $g < 3$, but SL is absent at these conditions (see fig.1);
- a glow at hit of a jet into liquid surface is absent.

So, nowadays only the theory of local electrification can explain the data on a glow of deformed laser bubble.

From these points we can conclude that the form of a cavitation bubble is the fundamental characteristic. Accordingly to experimental data [12,13], the extreme parameters, that could be reached at bubble collapse, are strongly decreased even at small deformation of bubble surface. Accordingly to [12], for cavitation bubbles near a solid surface the critical value $g_{cr} / 4.7$ and light emission from the bubble center is absent (the glowing region is localized near bubble surface, fig.2). Now we turn to the case of acoustic cavitation and consider interaction between two bubbles. To obtain the same parameters inside the bubbles as in the case of system bubble – solid surface, we should obviously lay the distance between them equal to $2l$. So, at least for moderate sound intensities, we can estimate the cavitation index K_{cr} (K is the ratio summar volume of the bubbles at maximum expansion to the volume of cavitation field [14]) at which bubble deformations lead to absence of high temperatures:

$$K_{cr} = (2\gamma_{cr})^{-3}$$

For water we obtain $K_{cr} \in 1.2 \cdot 10^{-3}$. This value seems to be underestimated for acoustic cavitation because of at least two reasons:

1. Maximum temperature inside the laser bubble at collapse is higher than that for acoustic cavitation bubble, that's why absence of high temperature in case of acoustic bubble take place at larger γ , than in the case of laser bubble. Really, average speed of laser bubble expansion is about 15 m.s^{-1} and it occurs much more than critical speed v_{cr} of condensation and evaporation of vapor inside the bubble (for water at 20°C one obtain $v_{cr} \approx 6 \text{ m.s}^{-1}$). So, at fast laser bubble expansion, liquid doesn't have time to be evaporated and at maximum expansion the vapor pressure is much smaller than saturated one. As to acoustical bubble, average speed of expansion is not too large ($1-3 \text{ m.s}^{-1} < v_{cr}$) and at maximum bubble expansion vapor pressure is about to saturated one. So, the following fast collapse will be damped considerably in the case of acoustic cavitation bubble [] and vice versa in the case of laser bubble.
2. We know only bottom limit for γ_{cr} . It can occur that real γ_{cr} would be about 9 and in this case K_{cr} will decrease by an order.

Accordingly to conclusions of Rosenberg [14], who the first has considered the influence of cavitation bubbles interaction on their extremal parameters, the most sizeable effect is bernoulli pressure, so, this interaction becomes important at $K_{cr} > 0,125$. But accounting of real deformations of cavitation bubble shows that real K_{cr} occurs smaller at least for two orders. Accordingly to numerous experiments, at regime of developed cavitation in water at moderate intensities K can vary from 10^{-2} to 0.9 [14] and **occurs much more than K_{cr}** determined here. The fundamental deduction is that even in weak multibubble systems interaction between bubbles is substantial and practically all cavitation bubbles are deformed and high temperatures inside them, which are sufficient to SL and sonochemical reaction arising, are absent. That's why lately interest to the heat theory decreases and this theory is not almost mentioned in grave reviews (see, for example, [12]).

The theory of local electrification now is a single one, which correlates with the majority of experimental facts on multibubble cavitation fields.

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