

Bubbles Induced Fluctuations of Some Properties of Aqueous Solutions

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Abstract—A mathematical model of the air diffusion process through the water surface taking into account the reverse flow of bubbles was proposed. The numerical solving gives self-oscillation of the dissolved air concentration. Spectral density of these oscillations has the $1/f$ -noise form, which explains the fluctuating nature of the observed properties of water and biological effects, which depend on the amount of dissolved air. A mechanism of spontaneous water luminescence observed after laser irradiation was suggested. The calculated luminescence self-oscillations have the form of a fractal with an infinite sequence of periods, which evolve in time and that is qualitatively consistent with the experiment.

Keywords: water, air, bubbles, diffusion, mathematical modeling, fluctuations, luminescence, fractal

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INTRODUCTION

Biological effects connected with the structure of water have recently been attracting special attention [1]. The results of many work point to a definitive role of the “water–air” interface both on the surface of water and in microbubbles, which spontaneously form in water, containing under normal conditions about 2 vol % of air. Investigations of the interaction of bubbles among themselves and with other materials, such as solid particles or drops of oil, serve as a basis of various technical applications—foam formation, treatment of food products, purification of waste water etc. Special interest is raised by the questions of structuring or activation of water under external influences. Thus the authors of work [2], having investigated the effects of electromagnetic fields (EMF) in triply distilled and deionized water, come to a conclusion that the field may act on the water-dissolved gas. The possible role of microbubbles in the processes of transformation of the energy of external influences has been discussed in works [3, 4]. According to [5], microbubbles of air can serve as primary targets of the influence of weak EMF on water and bioliquids. As a result of such influence the bubbles grow, which leads to degassing of the liquid. Degassing, in its turn, changes the physicochemical properties of the liquid, such as electroconductivity, acidity, transparency etc. [6]. A change in the properties of bioliquids, in essence, presents a cause of the

observed bioeffects [7]. Thus for example, degassing of blood plasma in vitro substantially influences the results of analyses [8–10].

Despite that a vast quantity of works have been devoted to investigation of the properties of water and water solutions (see, for example, [11]), at the present time there remain a series of unsolved problems. First of all, this is the problem of poor reproducibility of some experimental results, which is usually connected with uncontrolled changes in water structure. Interestingly, the observed fluctuations of the measured indices—luminescence intensity [12], ortho/para ratio [13], discharge rate of a condenser with water [2], electroconductivity of water [14]—possess characteristic periods from several seconds to several hours and even days, which is much greater than any molecular or supramolecular times that are possessed by water proper as a set of H_2O molecules.

The aim of the present work is to show that the observed fluctuations of water properties may be connected with chaotic oscillations of the concentration of water-dissolved air and quantity of microbubbles. These oscillations are conditioned by competition of a slow process of molecule diffusion from the atmosphere through the surface into the depth of the vessel and a relatively fast reverse process of degassing via birth, growth, and flotation to the surface of air bubbles. This out-flux is proportional to the accumulated amount of air in solution, which sharply decreased after exit of bubbles (or group of bubbles). Therewith the slow diffusion into the depth has no time to make up for the loss, which leads to lagging and in the final

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analysis to autooscillations, the frequency of which is random but possibly groups around some characteristic values determined both by conditions of the experiment, for example the dimensions of the vessel, and by uncontrolled external influences (weak electromagnetic or acoustic fields, oscillations of temperature and pressure) that influence the growth of bubbles.

MATHEMATICAL MODEL

Let us consider the diffusion of air molecules across the surface into the depth of a vessel with water taking into account the reverse flow exiting with bubbles, which spontaneously arise, grow and float to the surface. The processes of nucleation and stabilization of bubbles remain beyond the framework of the problem being solved. It is supposed that the growth of bubble volume is conditioned by variable external pressure and may take place by the mechanism of rectified diffusion [15] or through fusion under the action of Bjerknes forces. Alternating pressure arises as a result of thermal fluctuations, or else uncontrolled influences of acoustic or electromagnetic fields. In this way, the described process reduces to an equation for diffusion with sink into bubbles:

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} = D\Delta c(\mathbf{r}, t) + S(\mathbf{r}, t), \quad (1)$$

where $c(\mathbf{r}, t)$ is the concentration of dissolved air molecules in point $\mathbf{r}$ at time moment t , D — diffusion coefficient (average over all air components). Sink function $S(\mathbf{r}, t)$ in equation (1) describes the leaving of dissolved air into the gas phase inside bubbles, as a result of which the bubbles grow and float to the surface, taking air out of solution. Searching for this function is connected with solving the equation for diffusion from solution into the bubbles the coordinates and sizes of which change with time. This is a laborious enough task, which, however, can be significantly simplified.

Let R be the size of the region in which a change of concentration take places at the expense of air diffusion into a bubble. Considering that R is incomparably smaller than the depth of the vessel $z_{\max}$ ($R \ll z_{\max}$), one can avoid solving a three-dimensional problem. Let us leave outside the framework of our analysis the processes of nucleation and stabilization of microbubbles—this is a problem from a different area of far smaller time and space scales [16]. Let us take that an equilibrium concentration (pressure) of air in a bubble is established instantly and (by the Henry law) is proportional to the concentration in solution, inasmuch as the characteristic time of bubble saturation with air $t_b = R^2/D$ is much smaller than the characteristic time of vessel saturation $t_{\max} = z_{\max}^2/D$. Therewith the increment in volume of an i -th bubble $d\Omega_i$ is determined by the local diminution of concentration: $\partial c(\mathbf{r}, t)/\partial \Omega_i = -1$. In this approximation one may take

that $c(\mathbf{r}, t) \equiv c(z, t)$ is the concentration (or number of molecules) of dissolved air per unit length, the Laplace operator is simply the second derivative with respect to z , while $d\Omega_i$ is concentration (or number of molecules) in the layer of bubbles (also per unit length) at level z . Then the sink function can be written down in the form:

$$S(z, t) = \sum_{i=1}^{N(t)} \theta(t - t_i) \frac{\partial c(z, t)}{\partial \Omega_i} \frac{\partial \Omega_i}{\partial t}. \quad (2)$$

In equation (2) the contributions are summed over all $N(t)$ bubbles being present at time moment t in solution:

$$N(t) = \sum_i \theta(t - t_i) \theta(-R_i(t) - Z_i(t)), \quad (3)$$

where the coordinate θ -function cuts off all the bubbles having touched the water surface. The coordinate of the bubble center at time moment $t > t_i$ is determined by formula:

$$Z_i(t) = \int_{t_i}^t V(R_i(t')) dt' + Z_{i0}, \quad (4)$$

where Z_{i0} and t_i are place and time of birth of the i -th bubble. A bubble of radius R_{i0} appears at the given point at random with probability $dP(z, t) = pc(z, t)dt$, proportional to the concentration, and then floats up with velocity V , which, according to the Stokes formula, is proportional to its squared radius:

$$V(R) = AR^2. \quad (5)$$

For a sphere $A = 2g/9\nu$, where $g = 9.81 \text{ m s}^{-2}$ is acceleration of gravity, while $\nu \approx 10^{-6} \text{ m}^2 \text{ s}^{-1}$ is water kinematic viscosity. However in our case A remains a free parameter, compensating for the shortcomings of the chosen simplification of the problem. At that the bubble volume grows at the expense of air diffusion from solution with the rate proportional to its squared radius:

$$\frac{d\Omega_i}{dt} = 4\pi R_i^2 \mu_i(z) c(z, t), \quad (6)$$

$$\frac{dR_i}{dt} = \int_{-z_{\max}}^0 \mu_i(z) c(z, t) dz. \quad (7)$$

As said above, the increment in bubble volume at the expense of diffusion in the given layer (6) is proportional to its surface area and value of concentration. It is just this quantity summed over all bubbles in solution that determines the diminution of concentration in the given point z in equation (1). The total rate of change in volume and consequently radius of the bubble (7) is obtained by integration over all layers.

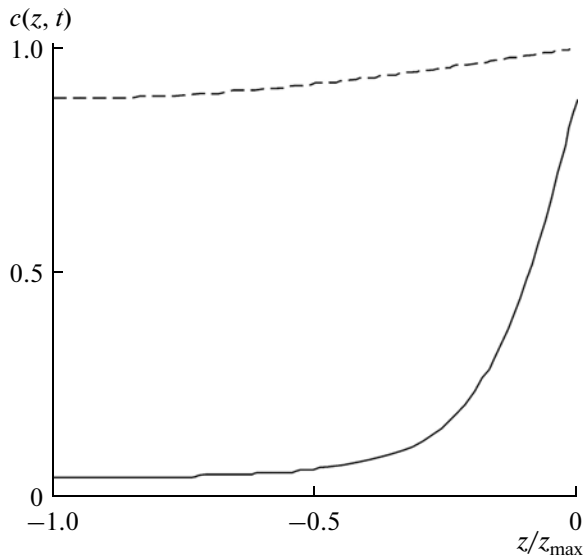


Fig. 1. Distribution of dissolved air concentration through depth $c(z, t)$ at $t = t_{\max}$ with account (solid) and without account (dashed line) of the exit of bubbles.

Factor $\mu_i(z)$ is chosen in the form of a normal distribution about the coordinate of the bubble center $Z_i(t_i)$:

$$\mu_i(z) = \mu_0 \exp\left(-\frac{(z - Z_i)^2}{R_i^2}\right), \quad (8)$$

in order to limit the region of sink to its vicinity nearest to the bubble center and to effectively take into account its three-dimensionality. The differential equation (6) describes the rate of growth of the i -th bubble centered in point Z_i , the position of which change by law (4). The thus obtained summand $S(z, t)$ in the right-hand part of equation (1) describes the diminution of concentration at the expense of transition of air molecules from solution to the gas phase into bubbles.

The initial and boundary conditions for equation (1) have the form:

$$\begin{cases} c(z, 0) = 0, -z_{\max} < z < 0; \\ \partial c(z, t) / \partial z = \frac{Bi}{z_{\max}} (c_{\max} - c(z, t)), z = 0; \\ \partial c(z, t) / \partial z = 0, z = -z_{\max}. \end{cases} \quad (9)$$

Here $z_{\max}$ — vessel depth, $c_{\max}$ — concentration above the surface, Bi — Biot number, the ratio of the surface diffusion permeability to the volume one (usually $Bi \sim 1$).

RESULTS OF CALCULATIONS

We will measure the distance in units of vessel depth $z_{\max}$, and time in units of characteristic diffusion

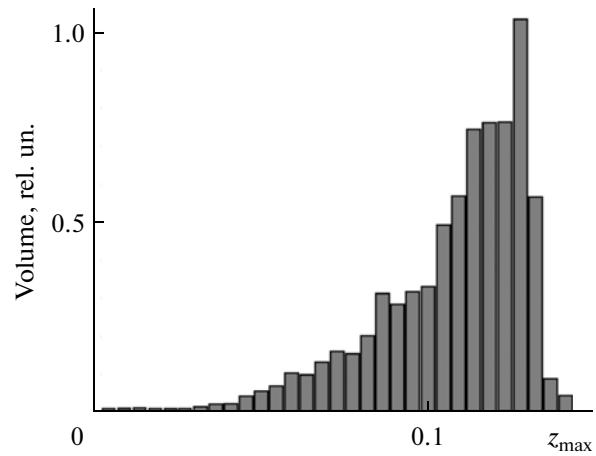


Fig. 2. Distribution of the sum volume of air having left by moment $t = t_{\max}$ with respect to bubble radius.

time $t_{\max}$. Therewith both the boundary conditions (9) with $c_{\max} = 1$ and $Bi = 1$ and the solutions of equation (1) do not depend on the choice of these parameters and diffusion coefficient D . The remaining parameters for numerical modeling were selected so as to obtain an effect with small time expenditures. Constant $A = 0.8 \times 10^4$, frequency of appearance of a bubble of minimal radius at unit concentration $p = 82$, $\mu_0 = 41$, step $dz = z_{\max}/128$, step $dt = 3 \cdot 10^{-5} t_{\max}$.

In Fig. 1 we present the results of calculating the concentration profile at moment $t = t_{\max}$. The dashed line is the result of usual one-dimensional diffusion with a boundary condition of third order at the outer surface. It is seen that without account of bubbles the system is close to equilibrium, inasmuch as $c \sim 1$ throughout the depth. The solid line calculated with taking into account the flotation of microbubbles lies substantially lower than the classical case.

The main contribution to degassing of solution is made by bubbles with radii largest at the given choice of parameters (see Fig. 2). Let us note that the notion of “bubble radius” in our approximation is quite conditional, inasmuch as in calculations the depth step dz and accordingly the minimal bubble radius are much larger than the real initial radii. In other words, the bubbles of ours are “demonstrative,” part of the history of their development is hidden in the parameter determining the probability of their appearance.

In Fig. 3 we present a dependence of mean depth concentration on time. The dashed line—usual diffusion—monotonically grows, while the solid line—calculation with bubbles—after an initial region of monotonic growth begins to chaotically oscillate about a value of 0.2. The same autooscillations must be exercised by all observed quantities the value of which is determined by the concentration of dissolved air. In Fig. 3 we can mark out characteristic periods, seemingly repeating throughout the entire numerical

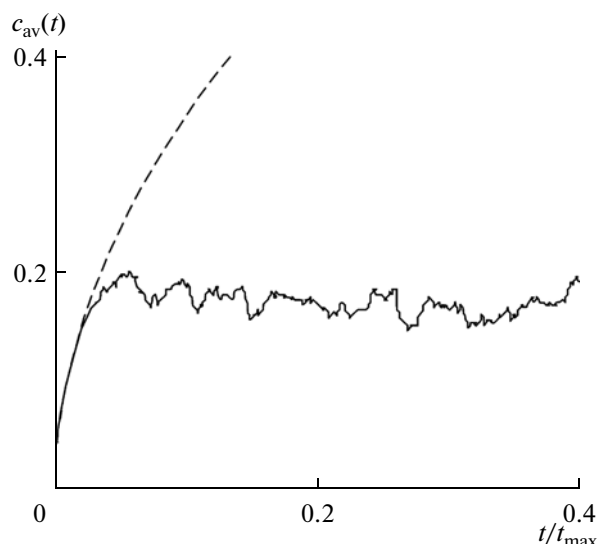


Fig. 3. Depth-average concentration c_{av} of dissolved air as dependent on time t with account (solid) and without account (dashed line) of the exit of bubbles.

experiment. However the results of Fourier analysis of the obtained oscillations (see Fig. 4) after multiple fluctuations upon increasing t in the process of calculation in the final analysis yield a monotonic curve corresponding to a characteristic dependence for $1/f$ -noise.

FLUCTUATIONS OF SPONTANEOUS LUMINESCENCE OF WATER

As shown in work [12], a five-minute irradiation with a low-intensity infrared laser ($\lambda = 1264$ nm,

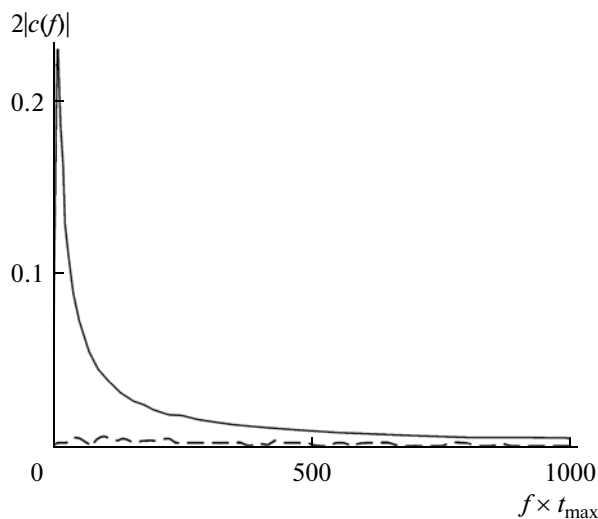


Fig. 4. Frequency spectrum of average concentration $2|c_{av}(f)|$ with deduction of the constant part with account (solid) and without account (dashed line) of the exit of bubbles.

power 5 mW) of air-saturated bidistilled water evokes with some delay (about two hours) autooscillations of spontaneous water luminescence in the blue-green region of the spectrum (see Fig. 5).

The nature of this luminescence is unclear, just as the cause of quasiperiodic fluctuations of the intensity of glow with periods of 5, 12 and more minutes. Wave analysis has shown that characteristic periods change in time. The authors of work [12] connect the water glow with excited states of infrared irradiation-formed radicals. It remains unclear whence comes the energy for excitation of transitions in the visible region of the spectrum and why the signal appears with a two-hour delay.

Let us try to clarify these questions, leaning on the above-presented results of modeling. Following [5, 7], let us presume that the luminescence-initiating infrared irradiation leads to water degassing, while uncontrolled external influences stimulate the growth of microbubbles. Let us assume that the source of glow energy appears as a surface energy that is liberated upon random collapse of bubbles in liquid volume, such a cavitation mechanism of spontaneous collapse of microbubbles was for the first time discussed in work [17]. Obviously, the cause hides in thermal fluctuations of pressure on the microlevel, analogously to the phenomenon of sonoluminescence [18], when pressure oscillations are created by an external source. Another possible mechanisms is liberation of energy at the moment of egress of the bubbles to the surface. This energy $E_s(R) = 4\pi R^2\sigma$, where $\sigma = 72$ erg cm⁻² is the coefficient of water surface tension, is quite significant even for the smallest bubbles. At $R = 50$ nm $E_{\text{surface}} = 362$ eV, which is about a hundred times

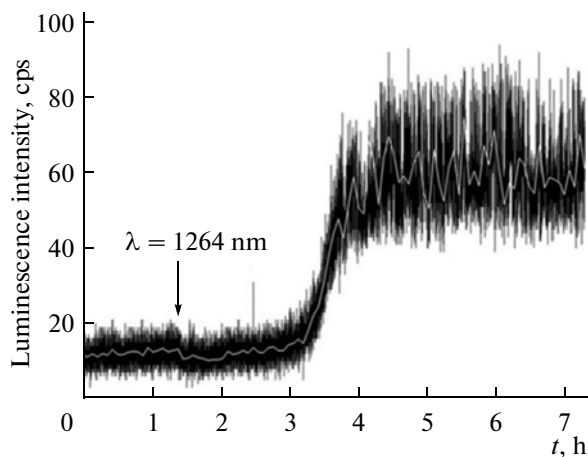


Fig. 5. The intensity of water luminescence before and after irradiation with infrared laser (moment of irradiation indicated by arrow), the light line is the result of smoothing (by the data of [12]).

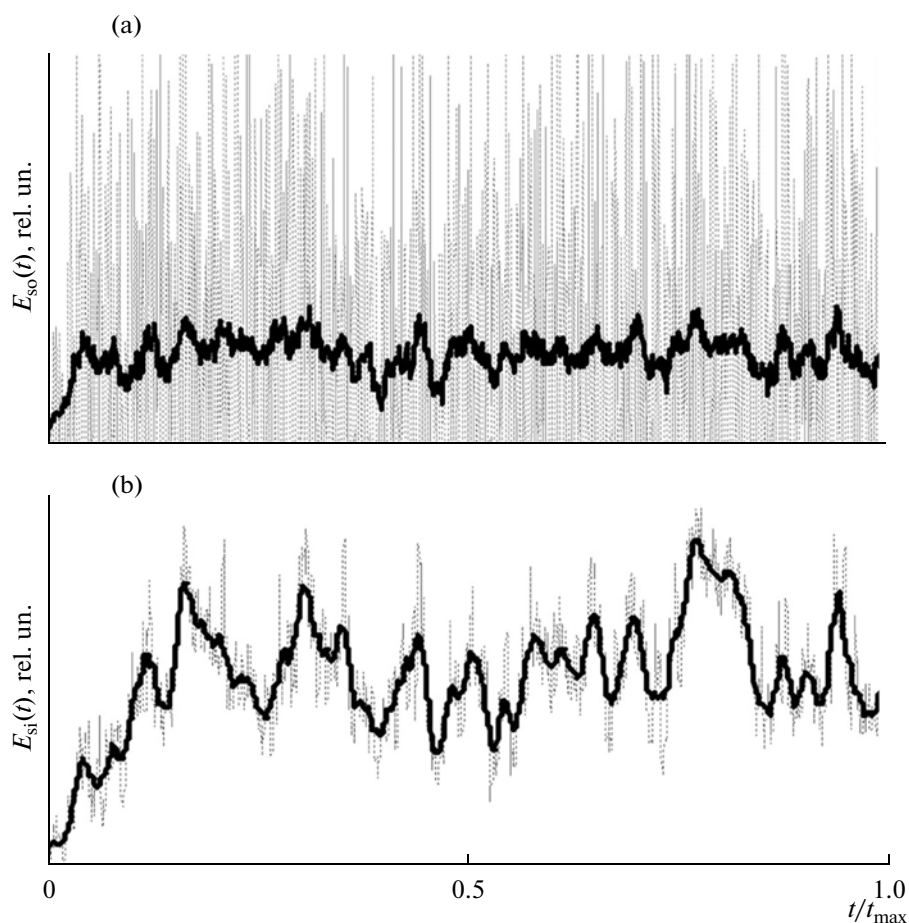


Fig. 6. Fluctuations of the sum surface energy of bubbles residing in the volume (bottom) and leaving the liquid (top), the bold line is the smoothed signal.

greater than the energy of quanta of the observed glow in the blue-green region.

Let us consider both ways of liberation of the surface energy of microbubbles E_{surface} . Obviously, the luminescence intensity will be proportional to the sum energy of the bubbles residing in the volume — $E_{\text{si}}(t)$, or exiting from the liquid — $E_{\text{so}}(t)$. For calculating the intensity it is enough to count the sum surface area of the bubbles residing in the volume or touching the surface per unit time, as dependent on time—this will be just our “signal.” The results of calculating such a signal are presented in Fig. 6, where gray dashed curves show the “instantaneous” values of the signal, black ones—the result of smoothing. Fluctuations of the signal, just as the fluctuations of concentration in Fig. 3, are determined by the random character of bubble exit.

As evident from Fig. 6, the signal appears with some delay, which is in accord with the results of experiment shown in Fig. 5, and is explained by the absence of bubbles at the initial moment. The fluctuations of functions $E_{\text{si}}(t)$ and $E_{\text{so}}(t)$ differ somewhat between themselves, which might serve as a criterion in comparison with

experiment and determination of the glow mechanism. At first glance, energy fluctuations in the volume of liquid (Fig. 6b) are more similar to the experimental picture (cf. Fig. 5). A large delay in our model is easy to obtain if we introduce a critical bubble radius R_c , beginning with which the collapse leads to glow. Before appearance of bubbles with $R > R_c$ the effect is simply absent, which is what is observed in experiment. However a detailed comparison with experiment was not among the tasks of the given article.

For elucidation of the characteristic periods of signal autooscillations we conducted frequency analysis with the aid of fast Fourier transform of the signal. The results are presented in Fig. 7, from which it is evident that the frequency distribution of $E_{\text{so}}(t)$, as distinct from $E_{\text{si}}(t)$, has a series of thicknesses (or peaks). Possibly, these are the characteristic frequencies of autooscillations, the nature of which demands special analysis. This fact may also be used for comparison with experiment and choice of model, inasmuch as in the literature there are numerous indications of the existence of distinguished periods of fluctuations [12–14].

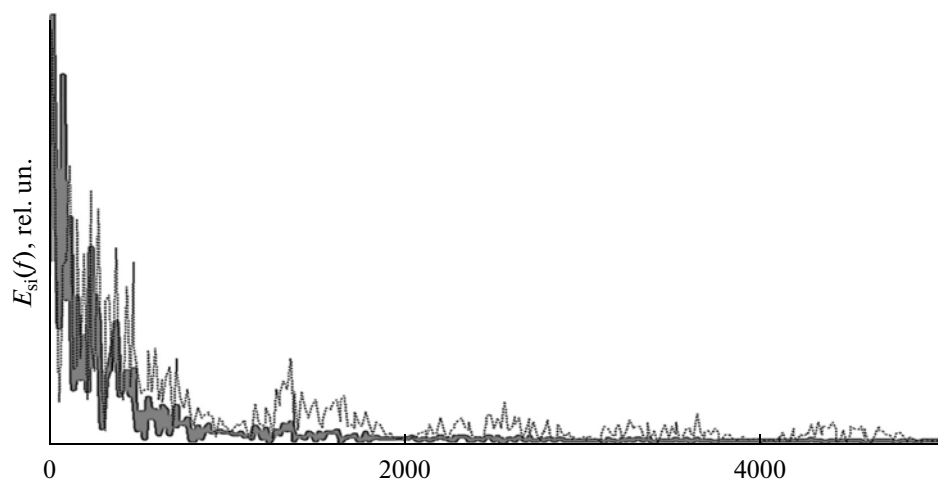


Fig. 7. Frequency spectrum of the fluctuations of the sum surface energy of bubbles residing in the volume (bold gray line) and leaving the liquid (dotted).

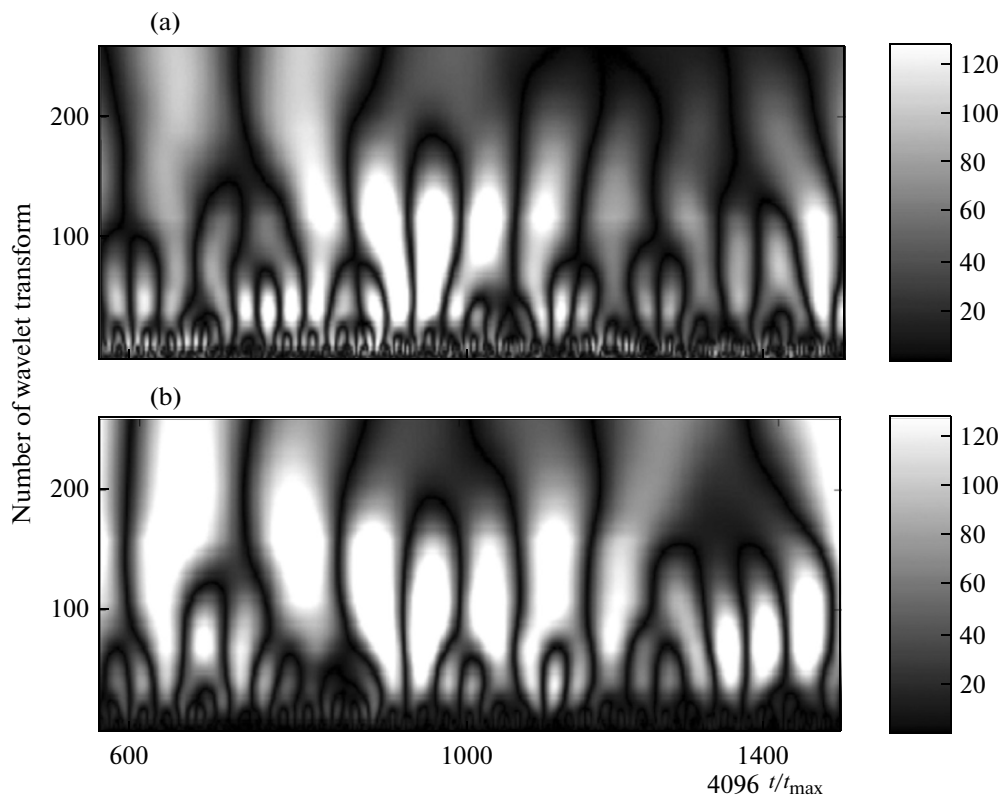


Fig. 8. Wave analysis of the fluctuations of the sum surface energy of bubbles residing in the volume (b) and leaving the liquid (a).

In Fig. 8 we present fragments of two-dimensional maps of coefficients of wave analysis on the basis of a set of harmonics *coif3* [19], well adapted for studies of fractal properties of signals. These coefficients, the magnitude of which is determined via the vertical scale on the right, reflect the degree of similarity of the corresponding harmonic and the analyzed signal.

As evident from Fig. 8, the picture repeats itself on different scales, which testifies to a fractal nature of these fluctuations. Apart of that, separate fragments of the distributions of coefficients for $E_{so}(t)$ and $E_{si}(t)$ are similar to each other, however there also are distinctions. The obtained maps qualitatively coincide with the one that is obtained upon analogous analysis with a

classical Koch's fractal curve. A small distinction consists in that in our case the characteristics of the fractal slightly evolve in time. In Fig. 8 one may perceive a change in time of the characteristic periods of fluctuation, which is consistent with the experiment [12].

In this way, we have obtained an explanation of the fluctuational nature and ambiguity of the results of measurements of those observed properties of water that depend on the quantity of air dissolved therein. Mechanisms are proposed for volume and surface spontaneous luminescence of water after irradiation with infrared laser, in which oscillations of luminescence are tied with autooscillations of the surface energy of bubbles. These oscillations have the appearance of fractals with a certain sequence of periods evolving in time. The fluctuations of the sum surface area of all bubbles $E_{\text{st}}(t)$ (Fig. 6) signify the same oscillations of the activity of own and admixed ions, inasmuch as these ions are adsorbed on the surface of microbubbles and thereby stabilize them [16], compensating for the Laplace pressure. Consequently, our model can explain the spontaneous oscillations of water electroconductivity observed in a series of works [14]. Let us note that the modeling conducted without any additional entities and fitting parameters shows a basic possibility of a simple enough physical explanation of some unusual properties of water. Possibly, a similar explanation exists also for "biorhythms," inasmuch as a fractal gives any desired "rhythm," while practically all biorhythms are fractal and therefore so adaptive to external influences.

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