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ACOUSTIC PROPERTIES OF GAS BUBBLES COATED WITH MONOLAYERS OF OIL SUBSTANCE[1]

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A gas bubble coated with a monolayer of oil substance, submerged in liquid, in the field of an acoustic wave is given theoretical consideration in this paper. Radial oscillations in the wave frequency band much below the resonance frequency depend mainly on the value of the monolayers modulus of elasticity and relaxation time t_r of the process of molecule reorientation which occurs in the monolayer due to its deformation. The following parameters were calculated: shift of the resonance frequency, damping constant of radial oscillations, and acoustic wave scattering and extinction cross-sections for a gas bubble in water, coated with a condensed monolayer of Extra 15 engine oil in angular frequency range $\omega \in [10^1 \div 10^5]$ rads^{-1} and range of radii of bubbles (3–50) μm. Predicted values of the damping constant and extinction cross-section in the wave frequency range $\omega < \alpha (\alpha = 2\pi/t_r)$ are by several orders of magnitude greater than those for a bubble with a clean surface. This effect is especially distinct in the case of microbubbles (with μm radii and smaller) placed at small depths (up to about 0.5 m).

Teoretycznym rozważaniom poddano pęcherzyk gazowy zanurzony w cieczy, pokryty monowarstwą substancji olejowej w polu fali akustycznej. W paśmie częstotliwości fali znacznie poniżej częstotliwości rezonansowej układu, drgania radialne zależą głównie od wartości modułu sprężystości monowarstwy i czasu relaksacji t_r procesu reorientacji molekuł zachodzącego w monowarstwie pod wpływem jej deformacji. Obliczono przesunięcie częstotliwości rezonansowej, stałą tłumienia drgań radialnych oraz przekroje czynne na rozpraszanie i ekstynkcję fali akustycznej dla pęcherzyka gazowego w wodzie pokrytego skondensowaną monowarstwą oleju silnikowego Extra 15 w przedziale częstotliwości kątowej $\omega \in [10^1 - 10^5]$ rads^{-1} i promieni pęcherzyków $(3 \div 50)$ μm. Przewidywane wartości stałej tłumienia i przekroju czynnego na ekstynkcję są o kilka rzędów wielkości większe od tych dla pęcherzyka o czystej powierzchni dla zakresu częstotliwości fali $\omega < \alpha (\alpha = 2\pi/t_r)$. Efekt jest szczególnie wyraźny dla mikropęcherzyków o promieniu μm i mniejszych usytuowanych na niewielkiej głębokości (do około 0.5 m).

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1. Introduction

Physical characteristic of many hydrodynamic systems with interfaces with an adsorbed film (foams, micro- and macroemulsions, gas bubbles) greatly depend on the modulus of elasticity of the surface monolayer [6, 16, 23]. Presented considerations concerning radial oscillations of a gas bubble covered with a monolayer of surface-active substance are based on Glazman's theoretical papers [11, 12]. Previous research on this problem disregarded the influence of monolayer's visco-elastic properties. This led to incorrect estimations of the resonance frequency of the bubble's oscillations or threshold of surface wave generation [2, 4, 10, 14, 15], for example. One of the authors previously investigated properties of monolayers of oil substances with various physical properties. These monolayers were formed on water surface [20]. It was possible to determine the influence of a condensed monolayer of light engine oil Extra 15 covering a gas bubble on the resonance frequency and damping constant of radial oscillations on the basis of these investigations. Dispersed in sea water oil-derivative substances can be accumulated for example on the surface of gas bubbles formed in the conditions of intensive wavy motion. This paper is also aimed at the determination of the influence of changes of the bubble's surface properties on acoustic wave scattering and extinction, and so on quantities directly deciding about conditions of wave propagation in a medium with bubbles. Presented results of theoretical considerations can be, applied in order to create a new effective method of evaluation of the water pollution based on bubble spectrometry [17].

2. Frequency of natural oscillations and damping constant of radial oscillations of gas bubble coated with adsorbed film

The classical Rayleigh's equation for oscillations of a gas bubble in liquid has been supplemented by GLAZMAN [11] with an additional term which includes visco-elastic properties of the adsorbed monolayer. The film decreases the average radius of an oscillating bubble in comparison to a clean surface, and as a consequence increases the frequency of natural oscillations. The ratio of frequency of free oscillations of a bubble with adsorbed film, ω_p, and a bubble with a clean surface, ω_0, is given by expression [11]

$$\omega_0/\omega_p = h\{[3kh^{3k} - W(h+3\beta h^3)]/(3k-W)\}^{1/2} \tag{1}$$

where: $h = R_0/\mathbf{R}$, R_0, $\mathbf{R}$ – equilibrium and mean radius, respectively, related by expression (30) in [11], k – polytropic exponent for the gas,

$$W = 2\gamma/(P_{i,eq} R_0) \tag{2}$$

is Weber number, $P_{i,eq} = 2\gamma/R_0 + 1.013\cdot 10^5\,(1+0.1H)$ – gas pressure inside the bubble, H – depth in liquid of the bubble, γ – interfacial tension,

$$\chi = -d\gamma/d\ln\Gamma \tag{3}$$

is modulus of elasticity of the monolayer discussed more fully in the next chapter [6, 16, 23], $\beta=\chi_0/\gamma$.

The damping constant B of the bubble's radial oscillation is expressed by a real and imaginary part of complex parameters $\tilde{\mu}$ and $\tilde{v}$ in the following form [12]

$$B=\omega^{-1}(\operatorname{Re}\tilde{\mu}-\tfrac{1}{2}\operatorname{Im}\tilde{v}^2), \tag{4}$$

where ω — angular frequency of acoustic wave, $\tilde{\mu}=(4\chi_0|\varrho\mathbf{R}^3)\eta/(1+\eta^2)$, ϱ — density of liquid,

$$\tilde{v}^2=(\varrho\mathbf{R}^2)^{-1}\left\{3kP_{i,eq}-\left(\frac{2\gamma}{R}\right)\left[1+\beta\left(3-4\frac{\eta^2}{1+\eta^2}\right)\right]\right\},$$

$$\eta=\alpha/\omega.$$

Parameter α is the angular frequency of relaxation processes of diffusion and reorientation of the surface-active substance's molecules in the monolayer due to changes of its area. The dimensionless damping constant δ (in the Prosperetti notation [22]) is related to the B constant in equation [8]:

$$\delta=2\beta\omega/\omega_0^2 \tag{5}$$

It consists of three terms responsible for losses due to: viscosity of surrounding liquid, heat conduction and acoustic radiation. Devin [8] thoroughly discusses the share of individual physical processes in oscillation damping of a gas bubble, and their value in the entire frequency range of the acoustic wave's field can be calculated from relationships given by Eller [9], Prosperetti [22] and Plesset [18].

3. Properties of adsorbed monolayers

A monolayer of surface-active substance is formed as a result of surface adsorption, described with Langmuir-Szyszkowski equations. These equations present relationships between surface pressure π and adsorption [7]

$$\pi=\gamma_0-\gamma=RT\Gamma_\infty\left(1+\frac{c}{a}\right), \tag{6}$$

and

$$\Gamma=\Gamma_\infty\left(\frac{c}{c+a}\right), \tag{7}$$

where γ_0, γ — surface tension for the solvent (water) and solution of the surface-active substance, respectively, R — gas constant, T — absolute temperature, c — molar concentration, Γ, Γ_∞ — adsorption and saturation adsorption, respectively, a — Szyszkowski's coefficient of surface activity.

Compression and dilatation of the area occupied by the monolayer causes adsorption changes. In accordance with Gibbs law [1] a periodical moleculae exchange between the monolayer and subsurface area occurs, as well as their reorientation in the monolayer itself (for insoluble substances). Both processes are characterized by definite relaxation times, t_r, related to parameter $\alpha (\alpha = 2\pi/t_r)$.

Limiting the problem to the diffusion process described by Fick's law, this time will have the following value [13]

$$t_r = \left[\frac{a}{\Gamma_\infty}\left(1+\frac{c}{a}\right)^2 \sqrt{D}\right]^{-2} , \tag{8}$$

where D — diffusion coefficient.

Table 1 in paper [21] presents t_r values for several chosen surface-active substances present in the subsurface layer of natural waters. They greatly vary depending on the molecular structure of the substance (length of the hydrocarbon chain, type, quantity and configuration of polar groups in the molecule). The diffusional interchange between bulk and surface during area contraction and expansion causes time dependent variations of the monolayer's modulus of elasticity which has a different value from determined by surface equation of state — $\gamma(\Gamma)$ (Equation (3)).

Table 1. Values of physical quantities used in calculations
*Data taken from [20, 21]

$P_{i,eq} = 101325$ Pa	$H = 0.2$ m
$T = 293$ K	$\gamma_o = 72.5$ m Nm^{-1}
$\varrho = 0.998 \times 10^3$ kgm^{-3}	$\gamma_0 < 47.5$ m Nm^{-1}
$R_0 = 3, 5, 30, 50$ μm	$^*t_r = 0.035$ s
$k = 1$ (for $R_0 = 3$ and 5 μm)	$^*\alpha = 179.1$ rads^{-1}
$k = 7/5$ (for $R_0 = 30$ and 50 μm)	$^*\chi_0 = 136.8$ m Nm^{-1}

Now it is expressed by [16]

$$\chi = \chi_0 (1 + 2\tau + 2\tau^2)^{-1/2} \tag{9}$$

where the diffusion parameter τ is equal to [16]

$$\tau = \frac{(c/a+1)^2 a}{\Gamma_\infty} \sqrt{\frac{D}{2\omega}}, \tag{10}$$

for monolayers obeying equations (6) and (7). The second type of relaxation observed for insoluble surface-active substances [3], can not be expressed by measured in macroscale parameters of the system on the basis of existing theories. Values of the α parameter for such monolayers (also oil) are determined on the basis of experimental measurements of their dynamic properties [16].

4. Oil monolayers

The author investigated monolayers of oil-derivative substances with varying physical properties, spread on water surface [20]. Light oil fractions such as gasoline 78, kerosene, diesel oil have low surface activity and the modulus of elasticity of their monolayers does not exceed 20 m Nm^{-1} at maximal compression ($\pi = 20$ m Nm^{-1}). While engine oils form "solid" type condensed layers, S [1]. The value of the modulus is equal to 93.6 and 136.8 m Nm^{-1} for Marinoll 111 oil and Extra 15 oil, respectively, at maximal compression of the monolayer. These values have been determined from separate physical and chemical measurements on the basis of relation $\gamma(\Gamma)$ (Equation (3)) obtained by means of Wilhelmy plate method [20]. One of the authors determined the α parameter for a monolayer of Extra 15 oil using the ultrasonic method of surface carpillary wave attenuation measurements [19]. The inflexion point of the wave attenuation coefficient versus frequency curve indicates the presence of a relaxation process at $f_r = 28.5$ Hz ($\alpha = 179.1$ s^{-1}) [21].

5. Gas bubble with oil monolayer

The knowledge of properties of oil substance monolayers on water surface [20] makes it possible to theoretically estimate their effect on oscillations of gas bubbles. Fig. 1 presents the ratio of the natural frequency of a gas bubble coated with a monolayer of Extra 15 engine oil in water, to the one of a clean bubble. It covers the entire range of surface pressures of the monolayer and was calculated from expression (1). Calculations were performed for two kinds of bubbles: $R_0 = 3$ μm (solid line) and $R_0 = 30$ μm (dashed line), placed 0.2 m under the water surface. The frequency increase effect is especially distinct for a microbubble in the range of high surface pressures. Then the modulus of elasticity takes values of about 10^2 m Nm^{-1} and the relative share of the capillary component W (Equation (2)) in the total pressure inside the bubble reaches about 0.4 at the depth up to 0.5 m. The following quantities: $\chi_0 = 136.8$ m Nm^{-1}, $\gamma = 47.5$ m Nm^{-1}, $\alpha = 179.1$, which characterize the Extra 15 oil monolayer on water surface at maximal compression ($\pi = 25$ m Nm^{-1}) have been introduced with the aid of expression (4) to the damping constant B beside quantities which characterize the liquid. Calculations (presented in

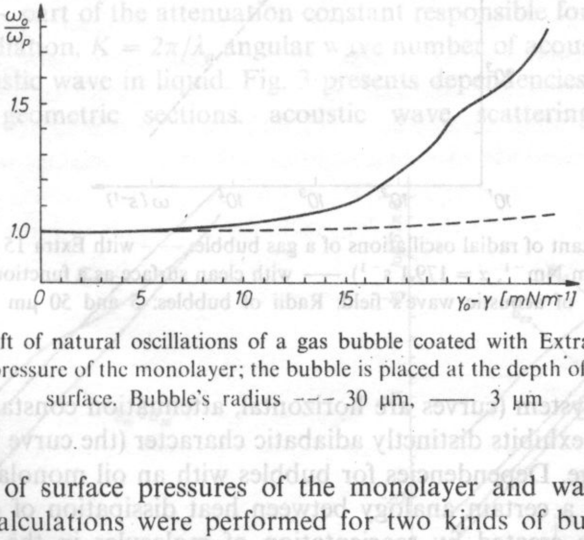

Fig. 1. Frequency shift of natural oscillations of a gas bubble coated with Extra 15 oil monolayer as a function of surface pressure of the monolayer; the bubble is placed at the depth of 0.2 m under the water surface. Bubble's radius --- 30 μm, —— 3 μm

graphical form in Fig. 2) were carried out for bubbles with 5 and 50 μm radii (dashed line). Values taken by B for a clean bubble placed in water adjacent to the surface ($P_{i,eq} = 101\,325$ Pa and $T = 293$ K) have been illustrated for comparison by the solid line. The polytropic exponent was chosen equal to 1 and 7/5 for the microbubble and a larger bubble respectively, [11]. A frequency range of the acoustic wave from 10^1 to 10^5 s^{-1} was chosen. Heat conduction causes main energy losses of the gas bubble in this frequency range [5]. Dependencies for clean bubbles indicate isothermal character of the system (curves are horizontal, attenuation constant-maximal); only the larger bubble exhibits distinctly adiabatic character (the curve begins to drop) in the kilohertz range. Dependencies for bubbles with an oil monolayer are of similar character. Hence, a certain analogy between heat dissipation of oscillation energy and energy losses created by reorientation of molecules in the oil monolayer is indicated. If the rearrangement process is quick enough in comparison with the characteristic time (period of acoustic wave) then the horizontal part of curves simulates the "isothermal" bahaviour of the system. The point of inflexion occurs at the frequency corresponding to the relaxation time of the reorientation process and to the transition of the system to "adiabatic" behaviour. At higher frequencies the oil monolayer becomes a less and less effective place of oscillation energy losses and the damping constant drops to zero. A difference of many orders of magnitude of B values between a clean bubble and a coated bubble proves that in the case of

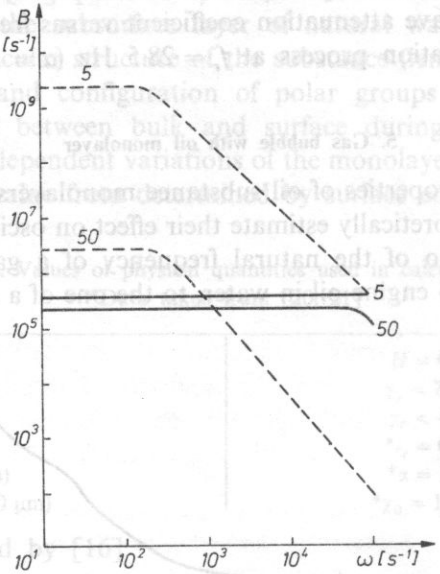

Fig. 2. Damping constant of radial oscillations of a gas bubble: --- with Extra 15 oil monolayer ($\pi = 25$ m Nm^{-1}, $\chi_0 = 136.8$ m Nm^{-1}, $\alpha = 179.1$ s^{-1}) —— with clean surface as a function of angular frequency of acoustic wave's field. Radii of bubbles: 5 and 50 μm

microbubbles and in the acoustic wave's frequency range $\omega < \alpha$ the molecule reorientation process in a monolayer of oil substance decides about the energy loss of oscillations.

6. Acoustic wave scattering and extinction cross-sections

The average radius, resonance frequency and damping constant decide about propagation conditions of an acoustic wave in a bubbly medium. Dependencies for acoustic wave scattering σ_s and extinction σ_e cross-sections, respectively for gas bubbles have the following form [5]

$$\sigma_s = \frac{4\pi \mathbf{R}^2}{\left[\left(\frac{\omega_0}{\omega}\right)^2 - 1\right]^2 + \delta}, \tag{11}$$

$$\sigma_e = \frac{4\pi \mathbf{R}^2(\delta/\delta_r)}{\left[\left(\frac{\omega_0}{\omega}\right)^2 - 1\right]^2 + \delta}, \tag{12}$$

where $\delta_r = K\mathbf{R}$ – part of the attenuation constant responsible for energy losses due to acoustic re-radiation, $K = 2\pi/\lambda_a$ angular wave number of acoustic wave in liquid, λ_a length of acoustic wave in liquid. Fig. 3 presents dependencies of calculated and normalized to geometric sections, acoustic wave scattering and extinction

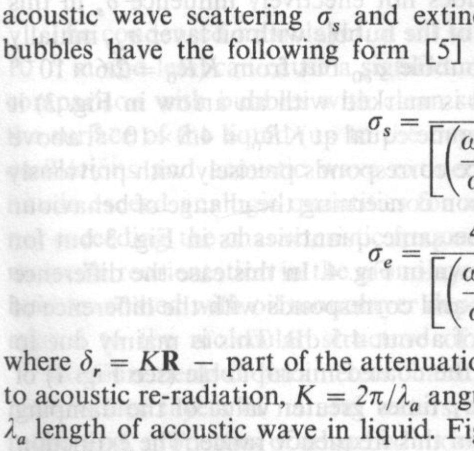

Fig. 3. Normalized acoustic wave scattering σ_s and extinction σ_e cross-sections for a bubble with clean surface "o" and a bubble with an oil monolayer "p" as a function of parameter KR_0 Bubble's radius – 50 μm. The arrow indicates the KR_0 value corresponding to acoustic wave's frequency $\omega = \alpha = 179.1\ \mathrm{s}^{-1}$

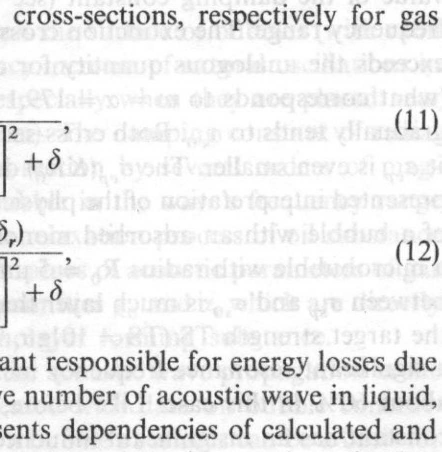

Fig. 4. Normalized acoustic wave scattering σ_s and extinction σ_e cross-sections for a bubble with clean surface "o" and a bubble with an oil monolayer "p" as a function of parameter KR_0. Bubble's radius: 5 μm. The arrow indicates the KR_0 value corresponding to acoustic wave's frequency $\omega = \alpha = 179.1\ \mathrm{s}^{-1}$

cross-sections for bubbles with a monolayer "*p*" and clean ones "*o*" with the same equilibrium radius $R_0 = 50$ µm, in terms of parameter KR_0. Physical properties of the liquid, properties of the Extra 15 oil monolayer, localization of bubbles and the wave's frequency range are the same as in previous considerations. Curves of scattering cross-sections are characteristic for Rayleigh scattering ($KR_0 \ll 1$) and the scattering function is proportional to $(KR_0)^4$ [5]. The difference between δ_{so} and σ_{sp} is insignificant. This result from the fact that the monolayer on a larger bubble causes only a slight frequency increase of natural oscillations (about 13%), and a greater value of the damping constant (see Fig. 2) does not effectively influence σ_s in this frequency range. The extinction cross-section of the bubble with oil layer σ_{ep} initially exceeds the analogous quantity for a clean bubble σ_{e0} but from $KR_0 = 2.6 \times 10^{-6}$ (what corresponds to $\omega = \alpha = 179.1$ s^{-1} and is marked with an arrow in Fig. 3) it gradually tends to σ_{e0}. Both cross-sections become equal at $KR_0 = 4.5 \times 10^{-5}$, above it σ_{ep} is even smaller. The $\sigma_{ep}(KR_0)$ dependence corresponds precisely with previously presented interpretation of the physical situation concerning the change of behaviour of a bubble with an adsorbed monolayer. The same quantities as in Fig. 3 but for a microbubble with radius $R_0 = 5$ µm are shown in Fig. 4. In this case the difference between σ_{sp} and σ_{s0} is much layer than before and corresponds with the difference of the target strength TS (TS = $10\lg\sigma_s/4\pi$ [5]) of about 4.5 dB. This is mainly due to a significant resonance frequency increase of the coated microbubble (see Fig. 1) of about 60% in this case. Like before, the many times greater value of the damping constant has an insignificant influence on σ_{sp} in this frequency range. The extinction cross-section σ_{ep} initially exceeds δ_{e0} over 10^3 times. However, for KR_0 exceeding 6×10^{-7} (what corresponds to $\omega = \alpha = 179.1$ s^{-1} and is marked with an arrow in Fig. 4) it gradually decreases and at $KR_0 = 1.6 \times 10^{-4}$ both extinction cross-sections become equal. Fig. 5 presents the σ_{ep}/σ_{0e} ratio for two kinds of bubbles as a function of the KR_0 parameter. In the range of KR_0 corresponding to

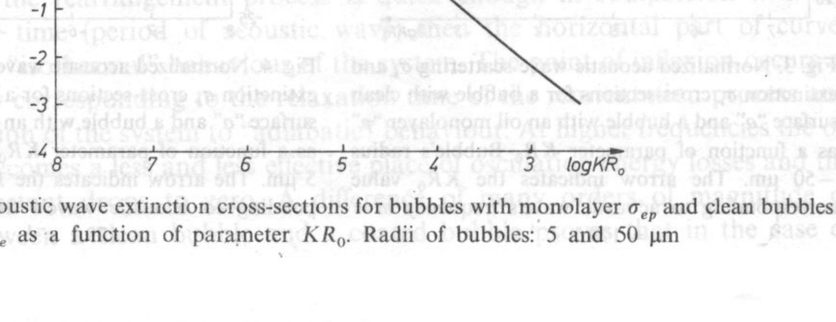

Fig. 5. Ratio of acoustic wave extinction cross-sections for bubbles with monolayer σ_{ep} and clean bubbles σ_{oe} as a function of parameter KR_0. Radii of bubbles: 5 and 50 µm

$\omega < \alpha$, the ratio is equal to 10^3 and 10 for a microbubble and larger bubble, respectively. The ratio decreases when frequency is increased and equals 10^{-1} and 10^{-3} for the highest frequency in the range under consideration. Presented relationships prove that viso-elastic properties of the adsorbed monolayer play a decisive role in the oscillation process. especially for bubbles with radii equal to several μm and localized near the surface.

7. Conclusions

The condensed monolayer of oil substance on the surface of bubbles (with radii 10^{-6} m and less) can cause a significant frequency increase of natural oscillations in comparison with bubbles with clean surfaces, especially when they are placed near the surface of the liquid (up to the depth of 0.5 m). The damping constant of radial oscillations and acoustic wave extinction cross-section by several orders of magnitude exceed analogic quantities for a clean bubble in the wave's frequency range not exceeding the characteristic frequency of the relaxation process of oil substance molecule reorientation in the monolayer. Actual values of acoustic parameters of gas bubbles coated with oil monolayer depend on quantities χ_0 and α, which are directly related to the molecular structure of the monolayer forming substance.

Measurements of parameters characterizing the acoustic wave propagation in the near-surface layers of natural waters, supplemented with data on bubble concentration and, properties of adsorbed monolayers on bubble's surfaces can be a basis for creation of a new effective method for the pollution evaluation of the sea water influenced by surface-active substances, including oil substances.

References

[1] A. Adamson, *Physical Chemistry of Surfaces*, John Wiley and Sons, New York 1976.

[2] A. M. Avenesov, I. A. Avetisyan, *Effect of polymer additives on sound propagation in water containing bubbles*, Sov. Phys. Acoust., **22**, 5, 359–370 (1976).

[3] R. L. Bendure, R. S. Hansen, *Damping of waves on monolayer covered surfaces*, J. Phys. Chem. **71**, 10, 2889–2997 (1967).

[4] M. Ceschia, R. Nabergoj, *On the motion of a nearly spherical bubble in a viscous liquid*, Phys. Fluids, **21**, 1, 140–142 (1978).

[5] C. S. Clay, H. Medwin, *Acoustical oceanography, principles and applications*, Wiley and Sons, London 1977.

[6] J. T. Davies, R. W. Vose, *On the damping of capillary waves by surface films*, Proc. Roy. Soc. London A **286**, 218–233 (1965).

[7] P. De Keyser, P. Joos, *Desorption at constant surface pressure from slightly soluble monolayers*, J. Colloid Interface Sci. **91**, 1, 131–137 (1983).

[8] C. Devin, *Survey of thermal, radiation and viscous damping of pulsating air bubbles in water*, J. Acoust. Soc. Am., **31**. 5, 1654–1667 (1959).

[9] A. I. Eller, *Subharmonic response of bubbles to underwater sound*, J. Acoust. Soc. Am., **55**, 4, 871–873 (1974).

[10] A. FRENCESCUTTO, R. NABERGOJ, *Pulsation amplitude threshold for surface waves on oscillating bubbles*, Acustica, **41**, 4, 215–220 (1978).

[11] R. E. GLAZMAN, *Effects of adsorbed films on gas bubble radial oscillations*, J. Acoust. Soc. Am., **74**, 3, 980–986 (1983).

[12] R. E. GLAZMAN, *Damping of bubble oscillations induced by transport of surfactant between the adsorbed film and the bulk solution*, J. Acoust. Soc. Am., **76**, 3, 890–896 (1984).

[13] P. JOOS, G. BLEYS, *Desorption from slightly soluble monolayer*, Colloid Polymer Sci., **261**, 12, 1038–1042 (1983).

[14] W. LAUTERBORN, E. CRAMER, *On the dynamics of acoustic cavitation noise spectra*, Acustica, **49**, 4, 280–287 (1981).

[15] S. P. LEVITSKII, *Dissipation effects with pulsations of gas bubbles in viscoelastic polymeric liquids*, J. Appl. Mech. Theor. Phys., **20**, 1, 74–79 (1979).

[16] E. H. LUCASSEN-REYNDERS, J. LUCASSEN, *Properties of capillary waves*, Advan. Colloid Interface Sci., **2**, 347–395 (1969).

[17] H. MEDWIN, *Acoustical bubble spectrometry at sea*, in: Cavitation and inhomogenities in uderwater acoustics, Proc. 1st International Conference, Springer-Verlag, Berlin 1980, pp. 187–193.

[18] M. S. PLESSET, A. PROSPERETTI, *Thermal effects in the free oscillations of gas bubbles*, Ann. Rev. Fluid Mech., **9**, 2, 145–185 (1977).

[19] S. POGORZELSKI, B. LINDE, A. ŚLIWIŃSKI, *Capillary wave attenuation on a water surface coated with monolayers of oil-derivative substances*, Acoust. Lett., **8**, 1, 5–9 (1984).

[20] S. POGORZELSKI, *Investigations of processes related to the presence of oil-like substances on water surface with the acoustic method*, Ph. D. thesis, Gdańsk University, Gdańsk 1985 (in Polish).

[21] S. POGORZELSKI, *Radial oscillations of gas bubbles coated with a monolayer of surface-active substances in the near-surface sea layer*, Oceanologia, **25**, 53–63 (1988).

[22] A. PROSPERETTI, *Thermal effects and damping mechanisms in the forced radial oscillations of gas bubbles in liquids*, J. Acoust. Soc. Am., **61**, 1, 17–27 (1977).

[23] J. D. ROBB [ed], *Microemulsions*, Plenum, New York 1980.

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