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C H R O N I C L E

DISSERTATIONS

Ultrasound scattering for characterization of marine crude oil spills

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Laboratory and at-sea surface scattering measurements, for wind generated water surfaces covered with crude oil derivative films of well-defined and oceanographically relevant viscoelastic surface properties, were carried out using a directional acoustic system based on high-frequency forward specular scattering. In the light of the "specular point" scattering theory applicable to ultrasounds (and also to laser, sun glitter, and microwave surface probing) the scattering coefficient of acoustic waves in these conditions i.e., for large values of Rayleigh parameter, depends only on the mean square slope of the rough surface. Water wave attenuation by a viscoelastic film is attributed to the Marangoni effect which causes a strong resonance – type damping in the short-gravity-capillary water wave region. The Marangoni damping depends on the physicochemical nature, concentration of the film-forming substance, and the rheological surface film parameters (E – elasticity modulus, P – film pressure, ω_0 – structural diffusion parameter). The scattered signal signatures turned out to be unequivocally related (via the Marangoni damping of wind waves by an elastic film) to the structural and rheological film parameters.

It has been demonstrated in open-sea experiments with artificial crude oil slicks spread over the Baltic Sea surface and a buoy-like free drifting low-weight acoustic system that the film parameters can be recovered from the ratio of the scattered signal low-frequency modulation spectra (with to without films) adopting a theoretical form of the relative spectrum with terms responsible for the Marangoni damping of wind waves, their growth, and spatial film homogeneity (i.e., film-filling factor). The latter parameter, which is wind-speed dependent, plays a principal role in the proper determination of the film properties derived, whereas a variation of the wind waves growth rate, also affected by the film presence, is of secondary importance.

The acoustically determined viscoelastic surface properties of a model slick are in moderate agreement with these simultaneously evaluated "in situ" using a novel film

sampler-elastometer-Langmuir trough system, and are characteristic of a natural slick of biogenic origin and/or "weathered" crude oil spills. A discrepancy between the acoustically derived and theoretically predicted relative spectra of wind waves is believed to result from a simplified model of the wind-wave interaction and a very complex form of fine structures of "real" wind-generated surfaces (parasitic, instability waves known as "cat's paws"), which may not express itself correctly in the signatures of the "specular point" scattering applicable to ultrasounds. The elastic properties of composite sea surfaces likely to be found in polluted coastal waters and consisting of oil spills filled with a surface-active material, floating solid particles (dust), gas bubbles, or drops of a third fluid with their important implications in remote sensing techniques are also discussed.

The statistics of the scattered signal fluctuations are approximated by expanding the Gaussian function into a Gram-Charlier series, taking into consideration statistical moments up to the fourth one. Evolution of the shape, skewness, and kurtosis of the signal distribution reflects an important role played by the film elasticity. Simultaneous analyses of all the statistical parameters could be a starting point for determining the fraction weight of the given spill-forming substance its layer thickness, and finally a form of the pollutant (monolayer, thick layer, or individual dispersed spots). The system allows the passage of the edge of the oil spill to be detected, and can provide significantly better resolution in the study of small spatial-scale air-sea interaction processes taking place at the sea surface than radar, and may be more convenient to operate in long-term continuous monitoring and less costly to use.

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Acoustical spectroscopy of cyclic and heterocyclic compounds, ketones and polluted water surface

Doctor Thesis (Dissertation 1997)
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THE CONTENTS OF THE THESIS

The subject of this thesis was the research of ultrasonic waves interaction with liquid molecules of pure organic compounds, solved in the other ones or spilt on the water surface.

There were two main aims of this thesis:

1) mainly on the basis of own acoustic investigations however enriched with some data taken from literature, concerning ultrasound absorption in ketones, cyclic and heterocyclic compounds, the author would like to established certain strict relations between acoustical absorption (α/f^2) rel and the molecules structure of a given liquid, and moreover to study some pure organic liquids and liquid mixtures with Kneser relaxation;

2) looking for the remote system in order to identify and control the ecological condition of seas as the first step in checking of oil pollution on surface of water.

As a consequence the work was divided into two parts: the first "A" – "Acoustic investigations in cyclic & heterocyclic compounds & their mixtures as well as some ketones", and the second "B" – "Amplitude spectrum statistical analysis of the acoustic wave, reflected from the undulated water surface, for identifying its pollution".

All results of investigations presented in this work are closely related to interactions of ultrasonic waves and the molecules of liquids.

The results presented in the I-st part of the Thesis has allowed the author to make following conclusions:

There exists a strict relation between acoustical absorption, in the frequency range below the Kneser relaxation process, and molecule structure. It closely depends on: numbers of the groups attached to the benzene or pyridine ring, the size of the group attached, the kind of the atom in the benzene ring, saturation of the compounds, numbers of the vibrational degrees of freedom as well as their distribution. The acoustical absorption dependence on aromacity and compressibility is rather ambiguous. There is no special relation between absorption and dipole moment.

The author has found the Kneser acoustical relaxation in six new compounds.

The situation similar to the first case takes place also for the group of compounds in which an isomeric relaxation is observed. The acoustical absorption depends on the size of chemical group attached to the ketone group what is connected with the conjugation of the $C_1 - C_2$ bond and increasing of the rotation barrier. This dependence in saturated ketones is much weaker than in unsaturated ones.

In the mixture of two Kneser liquids of highly-absorbing and low-absorbing abilities, it has been shown that the energy transfer between two different molecules is more

probable than between the same. There appear fast T–V and V–V transfers which fastens the process of molecular deactivation, they shorten the acoustical relaxation time and decrease the absorption coefficient α/f^2.

Referring to the II-nd part of the Thesis one may conclude that follows:

The measurements of the ratio of the measured spectra $D_r(f)$ or the acoustic amplitude pattern may enable the nature of the surface film to be characterised. It is of course difficult to deduce an exact physical and chemical nature of the sea surface films from the intensity and frequency of this characteristic peak, but it does seem feasible in principle to characterize surface films by this method. The direct influence of the surface film should be considered in terms of the chemical structure of the film's hydrophobic part of damping surface waves.

The attenuation of a surface wave propagated on the surface of water covered with an oil film attains values several times higher than those predicted by the classical hydrodynamic theory for a totally clean surface. The attenuation reaches its maximum, equal to $\alpha_{\max} \sim 2\alpha_{\text{imm}}$ (immo-bile), at low surface pressure. The maximum position is consistent with the prediction of the Dorrestein theory, however, it is lower and broader, due to the significant effect of viscosity. When the thickness of the film approaches or exceeds the generally assumed value which determines the depth of penetration of the undulatory motion $d \sim \lambda_b/2$, the values of the coefficient tend to approach the Stokes' expression α_m, exceeding it only by several per cent.

The observed instances of departure of a from the theoretical value are probably caused by the short distance between interfacial surfaces and the excessive viscosity of heavier fractions of crude oil, which leads to the unfulfilment of the applicability condition of the Stokes' approximation for an ideal liquid.

The stabilizing properties of the water surface covered with a monolayer of crude oil derivative and under the influence of an air stream depend on the type of derivative and surface concentration. A decisive role in the stabilisation process is being played by expansion surface elasticity ε_d of the monolayer. For strictly defined values of surface concentrations of the mono-layers of the investigated substances, the stabilisation of flow on the surface attains a maximum value.

Surface concentrations of monolayer, for which a maximum of surface capillary wave attenuation is observed, are very close to the values predicted by the theory for the maximum stabilisation. The agreement in the range of 30–55% indicates a close dependence between the process of wave energy dissipation and their formation under the influence of the air stream on the surface. The process is different for various viscoelastic properties.

The observed differences between both values of Γ results from a simplified and idealised model of the effect of the air stream on the liquid surface. The threshold air stream velocity capable of generating waves on the water surface covered by a monolayer of crude oil derivative is increased by a factor of about 18, while for the maximum achieved surface concentrations – by a factor of 5 – 7.5.

As far as the registration of the water pollution is concerned an acoustic high-frequency, surface scattering system consisting of the directional transducers of a narrow transmitting characteristic, is suitable to investigate the surface changes of an undulated

water caused by the presence of an oil substance layer. The statistical parameters of the echo peak value distribution from the rough water surface covered with the layer are markedly different from those for a clean surface. The changes of the parameters are of the order of several dozen percent for the normalized mean amplitude and fluctuation coefficient and the other parameters change by a larger factor, thus being more sensitive to the surface contamination.

On the basis of the results provided in natural condition (even open-sea measurements) carried out by means of free-floating (buoy-like) acoustic system all the laboratory observations presented here, as well as in many other our papers, were confirmed. Such an analysis of statistical properties of the acoustic field scattered at a rough surface can be a suggestion of a new, contactless method of remote sensing of surface pollution of natural water with oil substances.

Investigations of the finite amplitude wave propagation in water [in Polish]
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The aim of the thesis is the numerical analysis of the finite amplitude wave propagation in water. Following the description of the problem itself the physical model is presented and then the mathematical one. Further existing analytical solutions are discussed. The mathematical model is built on the basis of the KZK equation that describes the changes in acoustic pressure along the sound beam. Basing on the assumption that the wave source is circular and the amplitude of harmonic piston distribution is only a function of its radius the problem is considered as an axial symmetric one. The numerical methods must be used to solve the problem. Therefore usefulness of the choice of numerical methods is analysed. To solve this problem harmonic analysis, finite-element method and finite-difference method are applied. All these methods are described in detail. Own computer programs are worked out on the basis of obtained algorithms. Accuracy, convergence, influence of values of physical parameters such as for example nonlinearity parameter or dissipation coefficient of the medium and the fundamental wave distribution on the source (rectangular, polynomial and some different distributions which adequately simulate the real distribution on the source) have been investigated numerically. The calculations were carried out for different values of physical parameters and different values of parameters, which have influence on discrete model. The wave distortion and harmonic amplitudes evaluation as a function of the distance from the source on the beam axis and along the sound beam are studied. Moreover the average acoustic pressure on the receiving transducer is considered. The results of numerical calculations are compared with experimental ones.

On the near field of ultrasonically diffracted light [in Polish]

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Keywords: acousto-optics, near field (Fresnel region), far field (Fraunhofer region), intermediate diffraction regime, self-imaging phenomenon, secondary interference planes (Nomoto planes), KML method, NOA method, additional optical phase shifts.

The work is devoted to theoretical and experimental study of the Fresnel region of ultrasonically diffracted light. However some more general considerations are introduced yet the main interest is focused on the case of plane monochromatic light wave diffraction, incidenting normally a plane sinusoidal sound beam, propagating in transparent, uniform and isotropic medium (distilled water). The Thesis constitutes an attempt at analysis and recapitulation of nowadays state of the near field examinations as well as the experimental verification of the main theories describing the phenomenon of light diffraction by ultrasonic waves. In particular, the so called additional optical phase shifts (namely: initial phase shift and v-dependent phase shift), discovered and described in 1994 by P. Kwiek (Gdańsk University, Poland) and R. Reibold (PTB, Braunschweig, Germany), are under consideration and their influence over the secondary interference planes displacement is discussed.

Moreover, it is shown that while taking into account the complex character of the diffracted light amplitudes one can perfectly explain all the effects that, previously, have been attributed to the existence of phase-amplitude diffraction grating. Besides, a comparison is done of the results of the near field diffraction theory, given in 1976 by B.D. Cook with the ones making use of NOA method, proposed in 1987 by E. Blomme. The same, hitherto existing opinions have been revised, concerning B.D. Cook's theory correctness, by indicating limited range of its applicability.

It was also shown, that within the Klein–Cook parameter range under consideration, i.e. $0 < Q < 2.5$, there were no appreciable discrepancy between experimental data and the ones obtained by means of NOA method. Thus, no doubt that, at any rate within this range of the Klein–Cook parameter values, the NOA method is really powerful tool which provides us an excellent description of ultrasonic light diffraction phenomenon. Besides, it can be easily adopted for numerical calculations which, at least theoretically, can be carried on with unrestricted accuracy.

However, one should keep in mind that NOA method is in fact an approximative one and that at present there are no explicit and unequivocal opinion concerning the range of its validity. The experimental part of the work comprised near field measurements based on three independent techniques: (i) direct one – with light detector placed immediately within the Fresnel region of diffracted light, (ii) by means of an additional lens, transforming the exit plane from the sound wave to the image plane containing photodetector, and finally (iii) the one based on the so called single photon counting technique.

The experimental setup was fully automatized and controlled by a PC computer via GPIB/IEEE488 interface. Adequate configuration of the apparatus used enabled the author to obtain 5% accuracy of the time-dependent near field light intensity distribution measurements. It is worth noting that similar or analogical quantitative results have not been mentioned so far.

The Thesis consists of 7 chapters and introduction describing the historical background of the acousto-optics roots and evolution, giving one also a wide bibliographical review. Chapter I defines the basic notions which are commonly used to describe the phenomenon of light diffraction by ultrasonic waves. It also includes a short characterization of the so called self-imaging phenomenon. In Chapter II a procedure is introduced starting from Maxwell equations and leading to the Raman-Nath equations system, while Chapter III reveals different methods usually used to find solutions to these equations. Chapter IV gives the detailed description of the Fresnel region of light diffracted by ultrasound. In succeeding subsections several diffraction cases are analyzed and periodical character of the near field is discussed. Besides, a sound field reconstruction procedure is mentioned, based on the information contained in the Fresnel region of ultrasonically diffracted light. In Chapter V the so called finite amplitude effects are discussed. Thanks to detailed analysis of considerations presented in this chapter, suitable experimental conditions were found, justifying the negligence of the mentioned nonlinear effects influence over the carried measurements results. Chapter VI contains the detailed experimental setup description, presents the results obtained as well their discussion and comparison with appropriate theoretical predictions. Chapter VII comprises conclusions and final remarks.

Surface acoustic wave propagation in selected phthalocyanine thin layers [in Polish]
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The aim of this thesis was a theoretical and experimental study of the surface acoustic wave (SAW) propagation in selected phthalocyanine thin layers from the point of view of their application in toxic gas sensors. The thickness of all the investigated layers was much smaller than SAW wavelength ($h \ll \lambda$). This is a case of small perturbations in the SAW propagation on account of the thin layer placed on a piezoelectric crystal surface.

The theoretical study was based on Auld's perturbation theory using the notion of surface impedance. In the work the influence of the mechanical and the electrical properties (conductivity, diffusion constant and electrical permittivity) of thin semiconducting layers for SAW propagation in a piezoelectric crystal was applied. It has been shown that for SAW propagation the main influence is exerted by slight changes of the surface mass loading and surface conductivity of thin phthalocyanine layers. These two phenomena (i.e. mass and electric loading of the crystal) are the base for designing toxic gas sensors in low-range concentrations with the use of sensitive organic layers (for instance various metalophthalocyanine complexes). The electric effect results from the interaction of the electric field associated with SAW with mobile charge carriers in the phthalocyanine layer. It has been found that there is a strong frequency dependence of the conductivity of thin phthalocyanine films. This phenomenon facilitated the acoustoelectric effect between the SAW electric field and the mobile charge carriers in thin films. The strong frequency dependence of the conductivity of thin phthalocyanine layers has been confirmed by direct electrical measurements using a Tesla VHF Bridge.

The sensor properties of various thin phthalocyanine films have been tested with use of the well-known experimental set of dual-delay lines. On a piezoelectric substrate (i.e. $LiNbO_3$ Y-Z) two identical circuits are formed to facilitate the propagation of the surface wave excited by means of interdigital transducers. Next, by sublimation in a vacuum in one of the paths a thin layer of metalophthalocyanine is formed. The free path of the crystal serves as a reference, permitting easy measurements of the arisen difference of frequencies. Five types of phthalocyanines (PbPc, CuPc, FePc, NiPc and H_2Pc) have been examined at various concentrations of toxic gases (NO_2, SO_2, CH_4 and NH_3). The best results have been achieved for the PbPc and NO_2 low concentrations (below 1 ppm in air at 70°C). The gases were batched with the use of mass flow controllers.

From the physical point of view it is essential that the influence of each above mentioned effect (mass and electrical) should be considered apart from its reaction to the interaction of the layer with gas. For this purpose a special experiment with a lot of measurements has been carried out. The very thin aluminium layer left in one of the acoustic paths reduced the electric potential associated with SAW to zero. The obtained results confirmed the theoretical study in the quality range. It also determined the approximate

mobility of the charge carriers in thin layers. For all the investigated phthalocyanine films the obtained values were in good agreement with other methods for amorphous structures dealt with in literature.