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PHYSICAL ACOUSTICS

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Possibility of Generation of Ultrasonic White Noise

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Yoshio Ishida
Professor of the Department of Applied Physics, Fukui University.

Introduction

The construction of random processes in ultrasonic region is usually very difficult. However, the study of this work is very important because it is applicable to correlation techniques which are very useful for detection of hidden signal in noise.

Recently Proctor applied correlation techniques to ultrasonic inspection device. We attempt in this paper to generate ultrasonic white noise which can be used as a standard oscillator for random processes. The method proposed here to generate ultrasonic white noise is the electrical discharge system in electrolytic solution which has been used for the electrical discharge machining.

Method and Procedure

The method of electrical discharge machining includes the following physical meaning; a major part of the erosion by electric field force arise from the extremely high current density, the correspondingly high electric field gradient and the force on the positive ions of the crystal lattice; direct current discharges include the high frequency oscillations of electrons in glows and arcs, and low frequency electrical oscillations which have been associated with spark discharge.
Possibility of Generation of Ultrasonic White Noise

In this effect, we predict that electrical oscillations on the quartz plate causes generation of acoustic energy and such sound is propagating in the form of multiple longitudinal and shear modes. The experimental arrangement of electrical discharge system is shown in Fig. 1. This apparatus consists of platinum needle cathode 1 (0.51 mm φ, Pt-70% Ir-30%) and carbon anode 2 (10 mm φ). Surfaric acid 3 is contained in Polyacrylate discharge chamber 14, inner size of which is 90x90x20 mm. Discharge occurs between the platinum needle and the quartz.

In order to apply the constant weight between needle and quartz, the traveling microscope has a spring 7 (copper wire 0.5 mm φ, 27 turn, 50 mm long.) and a supporter 15.

A X-cut quartz disk (20 MC/S) with circular electrodes cemented the former quartz radiates the sound energy. It propagates through the distilled water 4 or the fused quartz rod (it is not shown in Fig. 1) and is received by transducer unit cell 8. This apparatus is supported with stainless steel rack 12 which is covered by the shield metal 13 to avoid the electromagnetic coupling.

| Ultrasonic Noise Generator | Frequency Converter | I.F Amplifier | Squaring Law Detector | Integrator Circuit | Meter Circuit |

Line filter are used in the source of electronic circuits.

Experiment and results

The block diagram of the equipment used to detect acoustic energy is shown in Fig. 2.

Acoustic energy which is generated by discharge systems are sent to frequency converter, I.F. amplifier, squaring law detector, and the meter circuit. The purpose of this electronics circuit is preparing for instrumentation of correlation technique after success of all systems.

In this paper, it was used for the observation of wave form.

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Possibility of Generation of Ultrasonic White Noise

Frequency range used are 20 - to 190 Mc/S. The wave form of I.F. output is shown in Fig. 3 - Fig. 6. These figures are photographs of synchroscope and show the spectra of ultrasonic noise. In Fig. 3 comparatively successive noise spectrum pattern are shown. In this case, the propagating medium is distilled water and path length is about 20 mm, discharge voltage is d-c 45 V, and needle length sunk into the electrolyticsolution is 3 mm. In this case, discharge state is comparatively stabilized. Fig. 4 indicates that discharge state is unstabilized. Intermittent discharge is caused when discharge state was transferred to the unstabilized state. In this case, the condition of discharge is d-c 75 V and propagating medium is fused silica rod. It was found that intermittent discharge consists of spectra with different duration and amplitude. Increasing the discharge voltage, duration time is varied and threshold ultrasonic noise is generated. (see Fig. 5, Fig. 6.)

In Fig. 6 reflected echo pulses are shown in different time. These correspond to the echo pulses from the end of the rod. In order to criticize the spectral characteristics, frequency analyzer is used. The discharge spectral characteristics are measured over the frequency range 1 - to 150 Mc/S. Each of the point in Fig. 7 represents the spectra of which discharge voltage is d-c 45 V, and d-c 75 V.
In the case of d-c 75 V, flat frequency characteristics are shown 2 - to 7 Mc/S and 40 - to 100 Mc/S. From 10 - to 40 Mc/S, it appeared that the amplitude of each point up to 20 db with frequency. Fig. 8 shows the characteristic of ultrasonic noise which is propagating into the water and the quartz rod. Because these data are insufficient to estimate ultrasonic white noise, statistical treatment has not been done. Finally, attention is focussed on the nature of discharge mechanism, wide use of transducer, and the development of correlation techniques of ultrasonic region. It is hoped that this work will be at least a step toward the generation of ultrasonic white noise and perhaps provide a stimulus for further investigation.

We wish to thank M. Tsubota for his variable assistance in preparation of this work.

Fig. 7 Frequency characteristics of discharge state.

Fig. 8 Frequency characteristics ultrasonic noise.

Reference

On the Excitation of Elastic Surface Waves with Wide Band Frequency Characteristics
Kimio Shibayama, Kazuhiko Yamanouchi and Takayoshi Hyodo
Research Institute of Electrical Communication, Tohoku University, Sendai, Japan

Introduction
The use of interdigital type electrodes on piezoelectric plates is effective for the generation of elastic surface waves. It is, however, not suitable to apply these electrodes to ultrasonic delay line systems, because the excited surface waves are limited within a certain narrow frequency band decided by the pitch of electrodes. In this paper, we discuss the behavior of the interdigital type transducers used together with an electromagnetic delay line in order to broaden the frequency bandwidth.

Frequency characteristics

Fig. 1 shows the schematic diagram of interdigital type transducers in our experiments, where electric signals are fed on each

![Diagram of interdigital type transducers and experimental arrangement.](image-url)
Excitation of Elastic Surface Waves

electrode from the corresponding terminal of the electromagnetic delay line. In this case, the phase velocity of the electromagnetic wave on the delay line is chosen to be equal to that of elastic surface waves along a crystal plate.

![Diagram](image)

*Fig. 2* Space distribution of electric fields.
(It is shown in the case of m=1 and n_p=5.)

To make the analysis easy, we assume that: i) There exists an infinite number of electrodes on a plate. ii) The electric field is simply given by (the terminal voltage impressed on a pair of electrodes)/(the interval of electrodes).

If the input signals are followed by \( e^{j\omega t} \) and the electromechanical coupling coefficient of the crystal plate is small, the space distribution of the voltage which acts on the electrodes becomes \( V=V_0 \cos \theta_y \), where \( h=2\pi/\lambda, \lambda=(n_p/m)\lambda_p, \lambda_p: \) pitch of electrodes, \( n_p \) and \( m: \) integer respectively. Consequently, as shown in *Fig. 2*, each electric field is represented by a rectangular form. In order to find the effective electric field \( E \) to yield the elastic surface wave, we expand the distribution of the electric field given by *Fig. 2* into Fourier series in the fundamental interval \( (0, n_p\lambda_p) \), and take the sum of all terms of \( m \), namely, of the corresponding terms of the propagation constant \( h \). Then we have

\[
E = \frac{V_0}{\lambda_p} \sqrt{\left[ \frac{\sin \left( \frac{m\alpha}{2} \right)}{m\alpha} - \frac{\sin \left( \frac{m\beta}{2} \right)}{m\beta} \cdot \cos \left( \frac{m\delta}{2} \right) \right]^2 + \left[ \frac{\sin \left( \frac{m\beta}{2} \right)}{m\beta} \cdot \sin \left( \frac{m\delta}{2} \right) \right]^2 \cdot \cos \left( \frac{m\theta_y}{2} \right) \cdots (1),
\]

where, \( m\theta=\alpha \), \( \alpha=2\pi(a/n_p\lambda_p) \), \( \beta=2\pi(b/n_p\lambda_p) \), \( \delta=2\pi(1/n_p) \),

(\( a \& b: \) interval of electrodes, \( d: \) width of electrodes in *Fig. 1*).

---

-H-6---
Excitation of Elastic Surface Waves

Examples of calculation results in Eq. (1) are shown in Fig. 3, in which curves correspond to the case $\alpha=0$, $\alpha: \beta=3:7$ and $\alpha=\beta$ respectively. The frequency $f_{E_{\text{max}}}$ which gives the maximum of $E^2$ depends on the ratio of $\alpha$ to $\beta$ and the width of electrodes $d$. When the $d$ takes $\lambda_p/2$, $f_{E_{\text{max}}}$ corresponds to $f_0$ given by the pitch of electrodes, where $f_0=V_s/\lambda_p$, $V_s$: the velocity of surface waves, and the narrower $d$ becomes, the lower the frequency $f_{E_{\text{max}}}$ becomes as seen in Fig. 4.

![Fig. 3 Frequency characteristics of the effective electric field.](image)

![Fig. 4 Dependence of the width of electrodes on $f_{E_{\text{max}}}$](image)

Experiments and their results

In Fig. 1, the signals of pulsed oscillation are given into input terminals. The corresponding output signals are led to an oscilloscope through a tuning circuit.

Experiment-1: We only put interdigital type electrodes composed of copper wires on a quartz crystal plate\(^1\). Consequently, the apparent width of electrodes looks very narrow. Dimensions are denoted in Table 1. The solid line in Fig. 5 shows the experimental result, in which the ordinate is in the relative

---
Excitation of Elastic Surface Waves

value of output voltage. The $f_{E\text{max}}$ appears in 1.5 MHz, and 6 dB down points in 0.7 MHz and 2.2 MHz, so that the bandwidth gives 1.5 MHz. The theoretical curve may be considered to be similar to the corresponding curve in Fig. 5. It may, therefore, say that the experiment is fairly well to the theory.

Experiment-2: Fig. 6 shows an example of evaporated electrodes on a quartz plate. The detail is also denoted in Table 1. In this case, $f_{E\text{max}}$ is situated in the neighborhood of 2.3 MHz. The theory also supports this result.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Data of experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment 1</td>
</tr>
<tr>
<td>$a\beta$</td>
<td>3:7</td>
</tr>
<tr>
<td>$\lambda_p$</td>
<td>1.75 mm</td>
</tr>
<tr>
<td>d</td>
<td>nearly zero</td>
</tr>
<tr>
<td>Number of pairs of electrodes</td>
<td>8</td>
</tr>
<tr>
<td>Delay time of electromagnetic delay line</td>
<td>0.53 $\mu$s/pitch</td>
</tr>
<tr>
<td>$f_0$</td>
<td>2.0 MHz</td>
</tr>
<tr>
<td>Quartz plates</td>
<td>X-cut: propagating direction of surface waves: Y-axis</td>
</tr>
<tr>
<td>Voltage insertion loss</td>
<td>65 dB (R=1.5 kΩ)</td>
</tr>
</tbody>
</table>

Through these experiments, therefore, it is expected to get a considerable broad bandwidth transducer for ultrasonic delay lines.

Acknowledgements

The authors express their thanks to Prof. K. Kamiyono and Dr. S. Ono of Tohoku Univ. for many helpful discussions.

Reference

Propagation and Detection of Elastic Surface Waves at GHz-Frequencies
E. Salzmann, T. Plieninger and K. Dransfeld
Physics Department, Technische Hochschule München, Germany

Rayleigh waves at microwave frequencies might become an interesting new tool for the investigation of surfaces in solid state physics. The absorption of Rayleigh waves, for example, could give valuable information about the superconductivity or about the magnetic properties of surfaces and evaporated thin films. In addition, it seemed important to study the intrinsic absorption of Rayleigh waves on surfaces of dielectric crystals which appears only at frequencies above a few hundred megacycles, which has never been observed before.

For these reasons we have attempted to generate Rayleigh waves at 1000 MHz by using a technique already described previously. Surface waves travelling on a y-surface of crystalline quartz into the x-direction were excited by a metal grating plated onto the surface. The r.f. electric field was applied between this grating and another counter-electrode underneath the quartz. Due to the strong inhomogeneous electric field and piezoelectric stress in the vicinity of the grating, Rayleigh waves are excited strongly if their wavelength is equal to the grating constant of 3u.

For detection of surface waves either the electrical 1) or a now
optical method was used. For electrical detection a second grating - at a distance of a few cm - was plated parallel to the first one (parallel within 1μ!). The voltage picked up from the second grating was fed into a heterodyne amplifier and displayed on an oscilloscope.

For optical detection we used the scattering of light by a Rayleigh wave. The beam of a He-Ne laser, incident from a denser medium at an angle α, was totally reflected from the quartz surface. As soon as a surface wave was present the reflection of the laser beam was no longer total, but a certain intensity was diffracted off into an angle β, depending on the surface wavelength. The intensity of the diffracted light, which is proportional to the intensity of the Rayleigh waves was simply monitored by a photomultiplier and the signal became larger as α approached the limiting angle of total reflection. The particular advantage of this optical method compared to others used at lower frequencies is the complete absence of a "zero-order" diffraction. Consequently there is no need for heterodyning the optical signal.

By probing the Rayleigh intensity at different parts of the surface, it is easy to determine the total attenuation of the Rayleigh
waves. From measurements at 300 MHz and 1000 MHz we found the attenuation to be 1 db/cm and 10 db/cm respectively (at room temperature) indicating an $\omega^2$-dependence.

The absorption of surface waves at lower temperatures was measured using the electrical detection. The resulting absorption is almost temperature independent between 300 °K and 60 °K, but at still lower temperatures the absorption falls as $T^4$. From measurements at 300 MHz and at 1000 MHz one can also determine the frequency dependence of the absorption: Below 60 °K it varies as $\omega^{1.4}$ in contradiction to the expectation for a three-phonon-process.

The absorption of surface waves is probably caused by their interaction with thermal bulk waves impinging on the surface. At high temperatures when the mean free path is shorter than the Rayleigh-wavelength $\lambda_R$, it is reasonable to expect a similar Akhiezer process known to be responsible for the absorption of bulk waves. At lower temperatures, however, where the mean free path of the thermal bulk waves is much larger than $\lambda_R$ the situation is less clear. Whereas the frequency dependence of the absorption was predicted by Mills and Maradudin to be linear, our observations seem to be in better agreement with an $\omega^{1.5}$-dependence. Further experiments are in progress.

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Ultrasonic Attenuation in Antiferromagnets

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**Antiferromagnet**

The magnetic properties of materials are expressed as the interaction of the magnetic moments of atoms with themselves and with externals. In a schematic way, the magnetic states are expressed by the arrangement of arrows in one-dimensional lattice as in the figure:

\[ \uparrow \rightarrow \downarrow \leftarrow \Rightarrow \cdots \]

The magnetic energy of the system is expressed as

\[ E_M = -J \mathbf{M} \cdot \mathbf{M} \cos \Theta \]

where J is the magnetic exchange integral, M is the magnetic moment and \( \Theta \) is the angle between adjacent moments. If J is positive, \( \Theta = 0 \) or parallel arrangement of M is stable and the energy is \(-JM\). This is the ferromagnetic state.

If J is negative, the stable state is \( \Theta = \pi \) or M is antiparallel and this is the antiferromagnetic state. In the antiferromagnetic state, opposite spins cancel each other and the magnetization do not appear. In general, the ordered arrangement of the magnetic moment is not limited in the above two cases but various types can exist, for instance

\[ \uparrow \rightarrow \downarrow \leftarrow \Rightarrow \cdots \ (\Theta = 45^\circ) \]

\[ \uparrow \uparrow \uparrow \downarrow \downarrow \downarrow \uparrow \uparrow \cdots \] (antiparallel at every three spins)
In these cases, the magnetic interaction is not limited in adjacent pair but extended to the second neighbour or more long distance. The simple antiferromagnet can be divided into two sublattices of upward and downward as in the case of the ordered binary alloy. In the body centered cubic lattice the unit cell is divided into two superimposed simple cubic lattice at the body center and the corner.

The elastic properties of the material can be expressed as an elastic interaction between atoms, the magnetic interaction between atoms can also contribute to the elasticity. In the magnetically ordered state the lattice deforms spontaneously and the elastic property becomes anisotropic. In a range of temperature close to the magnetic critical point, the magnetic state is modulated by the propagation of the sound waves. The energy of the sound waves is dissipated by a relaxation to the equilibrium state as a thermal energy. At the critical point of the magnetic materials, both the anomalous change of the elastic constant and the absorption of the sound energy will occur.

**Measurements**

MnF$_2$ is an antiferromagnet with the Néel point at 67$^\circ$K. The crystal structure is TiO$_2$-type and body centered tetragonal for Mn ions, the magnetic spins are in the c-direction. The sound velocity of the longitudinal waves along the [001] direction shows a large change at the Neél temperature. The elastic constant $c_{33}$ is shown in Fig. 1. The ultrasonic attenuation coefficient shows an anomalous increase around $T_N$ and the attenuation of the shear waves polarized in [001] direction is shown in Fig. 2. In some directions, an anomalous change of the elastic constant was observed. The difference in the elastic constant between the antiferromagnetic state and the paramagnetic state is the largest in the c-axis, this corresponds to the large magnetoelastic coupling in this direction.

CoO is antiferromagnetic and the Néel point is about 290$^\circ$K. An example of the sound velocity measured in a single crystal is shown in
Ultrasonic Attenuation in Antiferromagnets

Fig. 3. In this figure, the longitudinal wave was propagated along the [100] of the paramagnetic state, at $T_N$, a large jump is observed, corresponding to the large magnetoelastic coupling along the c-axis. The ultrasonic attenuation and the elastic constant were measured in magnetic field, an example is shown in Fig. 4. At $77^\circ$K, above 75 K0e both values become smaller. The magnetization shows a flopping at this field strength and the antiferromagnetic spin turns perpendicular to the magnetic field.

$\text{Cr}_0.1\text{Mn}_{1.9}\text{Sb}$ is antiferromagnetic below about 300$^\circ$K and ferromagnetic above this temperature. The elastic constant in the c-axis is larger in the antiferromagnetic state than in the ferromagnetic state. The magnetic spins are in the c-plane and the lattice constant along the c-axis jumps at the transition point. The magneto-elastic coupling has a large effect on the interaction of the magnetic spins.
Ultrasonic Attenuation in Antiferromagnets

Fig. 3. Elastic constant in CoO single crystal, longitudinal waves along the [100] direction of the paramagnetic state.

Fig. 4. Ultrasonic attenuation and the velocity of sound in magnetic field, at 77°K, shear waves along the [001] direction.

Fig. 5. Elastic constant of Cr$_{0.1}$Mn$_{1.9}$Sb along the c-axis, measured with longitudinal waves.
Magnetoelastic Signal Spectrum Modification by Adiabatic Magnetic Field Pulse.

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Taratorin U.A. - Student,
Krasilnikov V.A. - Professor,
Gontcharov K.V. - Candidate of science.
Moscow State University, Faculty of Physics.

The shape distortion of the magnetoelastic pulses generated under condition of the inhomogenious internal magnetic field $H_i$, amplitude pulsation, etc can be connected with the signal spectrum modification. Spectrum modification of the signal travelling as spin and magnetoelastic waves in magnetoinsulators, such as yttrium iron garnet (YIG) due to adiabatic pulse magnetic field effect has been observed recently (see Ref. [1-3]). It would be shown that the Dopler shift effect follows strictly from the continuity conditions of quasiharmonic wave in the space and timevarying dispersive medium.

The medium under consideration has phase velocity $V(z,t)$ depending on the space and time coordinates, which is due to the adiabatic external effect, and that perturbation travels with the velocity $V^\theta$. Supposing the phase velocity change $\delta V \ll V$, let us use the condition of conservation of the number of cycles $\omega_f dt_f = \omega_o dt_o$, where $\omega_o$, $\omega_f$, are the wave frequencies before and after external effect, $dt_o$ - an increment of time at the point $Z_o$; $dt_f$ - an increment of time at the point $Z_f$, corresponding to the time change of the phase arrival at this point. As is known
Magnetoelastic Signal Spectrum Modification by Magnetic Field Pulse.

(see Ref. [4]), the change of quasiharmonic spectrum signal \( \delta \omega \) can be written as
\[
\frac{\delta \omega}{\omega} = -V_\beta \frac{\delta V}{V (V-V_\beta)}.
\]  
(1)
The whole frequency change \( \Delta \omega \) for a final phase velocity increment of the magnetoelastic wave can be found by the integration of Eq. 1. Supposing \( V_\beta = \text{const} \) we have
\[
\int_\omega^{\omega+\Delta \omega} \frac{d\omega}{\omega} = -V_\beta \int_{V_0}^{V} \frac{dV}{V (V-V_\beta)}
\]  
(2)
from which we find the Doppler shift \( \Delta \omega \) as
\[
\frac{\omega+\Delta \omega}{\omega} = \frac{1-V_\beta / V}{1-V_0 / V_\beta}
\]  
(3)
An analogical relation have been used in Ref. 3. In case of the spin wave, the phase velocity is equal to \( V(z,t) = \gamma H_i(z,t)/k(z) + Dk(z) \).
This value changes from the light velocity in the medium \( (V_\ell = c) \) to the sound wave velocity \( (V_s = V_0) \). The adiabatic wave velocity change may be caused by the magnetic pulse field increment \( \delta H_i(t) \) since
\[
H_i(z,t) = H_i(z) + \delta H_i(t)
\]  
for sufficiently small spin wave velocity increment we have:
\[
\delta V = \gamma \delta H_i - \gamma \frac{H_i}{k^2} \delta k + \frac{1}{2} \delta k^2
\]  
(4)
and
\[
\delta k = \frac{\omega}{V} \delta \omega - \frac{\omega}{V_0} \delta V
\]
The joint solution of (1) and (4) if \( \delta k^2 \ll H_i \) is given by
\[
\delta \omega = m \gamma \delta H_i, \text{ where } m = \left[1 - \frac{\delta k^2 V}{H_i V_0}\right]^{-1}
\]  
(5)
So there is linear dependence of frequency change on the value of the magnetic field pulse in the first approximation.

An experimental investigation of 0.5 - 1GHz magnetoelastic wave spectrum has been made on YIG samples oriented with [100], [110], [111], directions parallel to the propagation axis. The slow wave systems have provided the excitation of magnetoelastic waves in the sample in the wide frequency band without overtuning. The trapezoid 0.2 - 0.4 Mc/sec magnetic field pulse was parallel to the direction of internal magnetic field \( H_i \). The frequency band width of the receiver \( (\Delta f = 10\text{Mc/sec}) \) make it possible to get a clear record of frequency shifted components. The excitation and the detection of magnetoelastic waves was carried out by the met
usually employed in the variable delay lines [5]. This method provides the observation of echo pulses with equal time spacing determined by the velocity of purely elastic wave (see Fig. 1a). The variable delay time of the first pulse in this series is carried out mostly by the spin wave dispersion. Fig. 2 shows the observed spin wave spectrum. The greatest change of the spectrum has been observed on the magnetic pulse switched simultaneously with the spin wave tracing. There is also some broadening of the spectrum without magnetic pulse switching (by a few tens of Mc/sec). The broadening of the spectrum as shown in Fig. 2 accompanies some decrease of the curve maximum. An appreciable pulse shape distortion has been observed in the case when the magnetic pulse was relatively late for the beginning of the spin wave travelling. So the splitting of the spin wave pulse has been observed (Fig. 1b). Fig. 3 shows the equal levels in a time-frequency space. The time-depending spectrum consideration shows that the frequency decrease takes place at the time of back front magnetic pulse effect, i.e. on the condition when

\[ \frac{dH}{dt} = \frac{dH}{dt} \tau_f < 0 \]

where \( \tau_f \) is front duration. In fact according to Eq. (5), the frequency shift sign coincides with the sign of \( \frac{dH}{dt} \).

The beginning of frequency change apparently takes place at the time of spin wave generation when \( \kappa_m = \kappa_{em} \approx 0 \). The maximum frequency change dependence on the amplitude of magnetic pulse \( H_p \) is plotted at the Fig. 4. The linear dependence \( \alpha_f \) on \( H_p \) accords to Eq. (5), if we take into account demagnetisation factors.

5. Гончаров К.В., Участькин В.И. Труды V1 Всесоюзной акустической конференции Е1117, Москва, 1968.
Magnetoelastic Signal Spectrum Modification by Adiabatic Magnetic...

Fig. 1. Oscilloscope traces of detected video output pulses series
a. $H_p=0$, $f_g = f_o = 712$Mc/sec,
b. $f_o = 712$Mc/sec, $f_g = 737$Mc/sec.
Left pulses in the dufes exists under $H_p=0$.

Fig. 2. The plot of the transduction losses versus frequency for the first magnetoelastic echo. 1-$H_p = 0$, 2-$H_p = 14800e$, $f_o = 850$Mc/sec, $H_o = 15000e$.

Fig. 3. The amplitude of shifted frequency signal for different levels versus time delay. $f_o = 850$Mc/sec, $H_o = 14880e$.
1 - $A = 120$db, 2 - $A = 100$db, 3 - $A = 95$db.

Fig. 4. Plots of negative frequency shifts against the pulse amplitude of magnetic field $H_p$:
$H_o = 15100e$, $f_o = 850$Mc/sec, 1-$\vec{E}||[110]$, 2-$\vec{E}||[111]$, 3-$\vec{E}||[100]$, where $f_o$ - the detection frequency.
Absorption of Ultrasound in Gadolinium Single Crystal Near Curie Point.

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The general phenomenological theory of Landau-Khalatnikov takes into account only lower order terms in the extension of thermodynamical potential $\Phi$. This theory determines the relaxation time near the point of phase transition of the second kind:

$$\tau = \left[ \tau_1^{-1} + \tau_0^{-1} \right]^{-1}$$

(1)

where $\tau_0 = 1/2k\alpha = \tau_{oo} \left( 1 - \frac{T}{T_c} \right)^{-1}$; $\alpha = \alpha'_T \left( T_c - T \right)$ is the coefficient in the dipole term in $\Phi$ - extention, $\kappa$ some kinetic coefficient. A maximum of sound absorption $\sigma$ according to the theory of relaxation [2] should be at the temperature for which $\omega \tau \approx 1$, since

$$\sigma = \frac{\Delta E}{2\nu \omega^2 \tau}$$

(2)

where $\Delta E$ is relative increment of the module of elasticity while passing through the Curie point; $\nu$ the velocity of sound. Thus the point of maximum $\sigma(T)$ proves to be shifted from the Curie point $T_{max} = T_c - \omega/2k\alpha'_T = T \left( 1 - \omega \tau_{oo} \right)$

From Eq. (2) follows that we have $\sigma = 0$ at the temperature $T = T_c$.

It has been shown in Ref. 3 that in case of the ferromagnetic-paramagnetic transition $\tau_c = \frac{M_0}{kH}$, $\Delta E(H) = k\gamma^2 M_0^2 \sigma = \Delta E(0) \tau / \tau_0$.
where γ is the magnetoelastic constant, \( M \), the saturated magnetization, \( E \) the module of elasticity. For the ferroelectric transition \( \Delta E \) is proportional to \( T \) (see Ref.4), from where follows the coincidence of \( T_{\text{max}} \) with \( T_c \) for ferroelectrics.

The experiments confirm the presence of the anomalous absorption of sound near the points of phase transition. Such absorption has been observed in ferroelectrics [4], in the liquid helium under superfluid transition [5], with the antiferromagnetic transition near the Neel point [6] and others. It should be noted that the phenomenological theory apparently needs further corrections particularly in order to explain the behavior of \( \sigma(T) \) in the region \( T > T_c \), although that theory is qualitatively true. Then the mechanism of relaxation may be investigated by means of comparison with the experimental curves for \( \sigma(T) \).

The results of our experiments also show the presence of the anomalous absorption of longitudinal elastic waves in a region of the ferromagnetic-paramagnetic transition. The Gadolinium single crystal has been investigated which has been grown in the laboratory of Savitzki E.M. of Metallurgical Institute of the Academy of Sciences USSR [7]. A cylindrical Gd sample was 0.8 cm in diameter and 0.5 cm long; the length of crystal was parallel to the crystal axis C. A quartz crystals of X-cut with resonant frequencies 10 and 27 Mc/sec were used for excitation and detection of ultrasound. The transducers were sealed with epoxi resin on the end surfaces of crystal. The pulse technique was used (10, 27 and 81 Mc/sec) for the sound attenuations measurements; the pulse duration was less than 1 sec. The sample fixed on the thermostatic device was placed in the gap of an electromagnet with a view of magnetic field effect measurements.

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Absorption of Ultrasound in Gadolinium Single Crystal near Curie Point.

The measured dependences of the attenuation from temperature for the longitudinal sound waves are shown in the Fig. 1. One can see the many-fold increase of the sound attenuation near 14°C.From 14°C to 17°C the sound attenuation falls rapidly (The Curie point for Gd crystal is $T_c = 17°C$ according to Ref. 7), but above the point one can see some attenuation decrease too. This behaviour is described by the empirical formula $\sigma - \sigma_0 = |T_{max} - T|^{-n}$, where $n=1.0, \sigma_0=1.0 \text{ dB/cm}$ (for paramagnetic phase at 27 Mc/sec.); $n=0.6, \sigma_0=1.6 \text{ dB/cm}$ (for ferromagnetic phase at 27 Mc/sec.).

It is worth being noted that according to theory in Ref. 9

$\sigma \sim |T_t - T|^{-0.5}$. The dashed lines in Fig. 1 show the corresponding theoretical curves calculated from the Eq. (2) with $T_0=0.5 \times 10^{-10} \text{ sec}$, $T_1=\infty$, $\Delta E=0.14\%$ and $\nu = 3.2 \times 10^5 \text{ cm/sec}$.

The magnetic field affects the relaxation time and the parameter $\Delta E(H)$ according to Eq. (1) and (2). The experimental curves for $\sigma(T)$ (27 Mc/sec.) are shown in Fig. 2 for the magnetic field perpendicular to the propagation axis. The observed decrease of the attenuation pike confirms the prediction of the theory; thus for the fields 1000 and 2000 gauss one can calculate the values $T_1=12 \times 10^{-8}$ and $6 \times 10^{-8}$ sec. Some shift of the absorption maximum has been observed too, although this shift does not exceed the experimental error.

Thus for the temperature range $T < T_c$ the experimental behaviour of $\sigma(T)$ corresponds fairly well to the phenomenological description. However the observed decrease of $\sigma(T)$ above $T_c$ and the noticeable increase of $\sigma$ in the magnetic field in paramagnetic phase does not agree with the phenomenological theory. Similar relaxation absorption in paramagnetics in a magnetic field has been predicted by the quantum theory (see Ref. 8). From this point of view the calculations of Populard [9] are of interest, being applied
Absorption of Ultrasound in Gadolinium Single Crystal Near Curie Point.

to the both phases of the substance.
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Fig. 1. The dependences of the attenuation from temperature for the longitudinal sound waves in Gadolinium single crystal.

Fig. 2. The dependences of the sound attenuation from temperature in Gadolinium single crystal placed in magnetic field. The dashed curves are calculated from Eq. (1) and (2) with $\tau_c = \infty$ and $6 \times 10^{-8}$ sec.
Ultrasonic Attenuation in Superconducting Vanadium

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Introduction

As is well-known, one of the most interesting problems in superconductivity is the dynamical properties of type-II superconductors in the mixed state. The important theoretical contribution to such a problem has been done by Maki[1], who calculated the ultrasonic attenuation, thermal conductivity and surface impedance by taking account of the gapless effect in pure type-II superconductors in a strong magnetic field. The experiments on the ultrasonic attenuation[2] and thermal conductivity[3] in Nb, however, showed a discrepancy between the theory and the experiments, i.e., the density of states at the Fermi surface estimated by the ultrasonic attenuation and the Maki theory is much smaller than that estimated by the electronic specific heat.

In order to investigate whether this discrepancy is inherent to the pure type-II superconductors or due to the band-structure effect, we carried out an ultrasonic attenuation measurement in V which has been shown to be one of the pure type-II superconductors[4]. The ultrasonic attenuation measured as a function of the magnetic field has been analyzed by using the Maki theory[4]. It was found that in contrast to the case of Nb, the density of states thus obtained is much larger than that estimated by the electronic specific heat[4].

Experimental Procedure
Ultrasonic Attenuation in Superconducting Vanadium

Vanadium specimen used was a single crystal of the circular rod of 6.4 mmφ x 10 mm with the axis parallel to the [110] direction. After cutting the vanadium of 99.986 % purity obtained from Materials Research Corporation, the top and bottom surfaces were ground to be parallel and optically flat. The specimen was then annealed in a vacuum of 3×10^{-9} mmHg at about 1700 °C during 35 hours. The resistance ratio R(300 K)/R(4.2 K) was determined by the eddy current method as 60.

Ultrasonic attenuation was measured by the pulse echo technique using the longitudinal wave of 285 MHz. The data were taken as a function of the magnetic field between T = 1.62 K and 5.5 K.

Result and Discussion

The ratio of the attenuation coefficient in the superconducting state to that in the normal state, \( \alpha_s/\alpha_n \), is plotted against the magnetic field in Fig. 1. The magnetic field was applied parallel to the direction of the wave propagation.

According to the Maki theory\(^1\) \( \alpha_s/\alpha_n \) near the upper critical field, \( H_{c2} \), can be described by the formula

\[
\frac{\alpha_s}{\alpha_n} = 1 - C \left( H_{c2} - H_{\text{ext}} \right)^{1/2},
\]

where \( H_{\text{ext}} \) is the external magnetic field. The factor C is the function of the temperature and the magnitude of \( q \ell \), where \( q \) is the wave number and \( \ell \) is the mean free path of electrons. If we assume \( v_F \) (the Fermi velocity) = 1.77×10^{7} cm/sec and \( \ell_0 \) (the coherence length) = 450 Å\(^1\), we obtain \( \ell / \ell_0 = 2.33 \) and \( q \ell = 0.032 \) in the present specimen. The attenuation coefficients are plotted as a function of \( \left( H_{c2}(T) - H_{\text{ext}} \right)^{1/2} \) at \( T = 1.62 \) K in Fig. 2, which shows that the attenuation cannot be well described by eq. (1).
The density of states can be estimated by fitting the theoretical formula (1) to the observed result in Fig. 2. The magnitude of the density of states thus obtained at $T = 1.62^\circ K$ was $N(0) = 2.93 \times 10^{35}$ erg$^{-1}$cm$^{-3}$, which is 3.1 times of $N(0)$ estimated by the electronic specific heat$^1)$. This is in a striking contrast to the situation in Nb, where the density of states obtained by the ultrasonic attenuation was smaller than $N(0)$ estimated by the specific heat.

The factor $C$ obtained in the measurement are shown in Fig. 3 as a function of temperature. The theoretical value$^1)$ of $C$ at the superconducting critical temperature $T_c$, is $2.37 \text{ kOe}^{-1/2}$ if we use the value of $N(0)$ obtained at $T = 1.62^\circ K$. Therefore, the temperature dependence of $C$ is qualitatively described by the Maki theory$^1)$. The theory predicts that for $q^2 \ll 1, C$ decreases by about 40 % when the angle between $q$ and $H_{\text{ext}}$ is
However, the experiments did not show such an effect.

The temperature dependence of $\frac{\alpha_p}{\alpha_n}$ in the absence of the magnetic field was found to obey the BCS formula with the gap parameter $2\Delta(0) = 3.52$ kT$_c$.

It should be remarked here that (a) the Maki theory$^1$ can be applied to the metal with single band and spherical energy surface, and (b) the measurement of specific heat$^5$ of Nb and V has revealed the existence of two energy gaps in the transition metal. Therefore, the large discrepancies of the density of states in Nb and V might be due to the band-structure effect. Further investigations, both experimental and theoretical, will be required to clarify this point.

Acknowledgments

One of the authors (K.K) would like to express his thanks to Professor A. Ikushima and Professor F. Akao of Osaka University for their encouragements and helpful discussions.

References

Gradient-elastic Tensor in Alkali Bromide Crystals
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Introduction
The interaction of acoustic waves with nuclear spins in solids has been investigated by many workers especially on alkali halides\(^1\). In these crystals, acoustic waves produce time-varying electric field gradients at nuclear sites and induce transitions between the nuclear spin levels if the nuclei have electric quadrupole moments. When the strain due to the ultrasonic wave is sufficiently small, the field gradient produced by the wave may be proportional to the strain. Therefore we can define a tensor of the fourth rank \((S_{ijkl})\) connecting the field gradient with the elastic strain. In this experiment, we determined \(S_{11}\), the \((xxxx)\) component of the \(S\) tensor, at alkali and bromine nuclear sites in all alkali bromide crystals. Some quantitative discussions are given in connection with the interactions between ions in the crystal.

Experimental procedure
The samples used in this experiment are all single crystals and are cut in form of circular cylinder, the axis of the cylinder being parallel to [100] direction.

A Pound-Watkins spectrometer was used to detect nuclear magnetic
Gradient-elastic Tensor

resonance (NMR). A quartz transducer was attached to one end of the crystal, which generates ultrasonic waves of about 15 m/s. The exact frequency was so chosen as to produce mechanical resonance in the crystal. The frequency of NMR was adjusted to be just half of the acoustic frequency. Thus, in an appropriate external magnetic field, the NMR signal corresponds to the transition $\Delta m = \pm 1$, while the acoustic wave induces the transition $\Delta m = \pm 2$. Here $\Delta m$ is the change in the magnetic quantum number of the nuclear spin. When the intensity of the acoustic wave was increased, the NMR signal showed a saturation effect. All the measurements were done at room temperature.

The absolute value of the strain in the crystal was determined by the measurement of the quality factor of the mechanical resonance (2).

**Calculation of the $S_{11}$ component from the experimental data.**

The intensity, $A$, of NMR when longitudinal waves propagating in the $x$-direction induce the transitions is given by (3)

$$A/A_0 = a/(1 + kE_{xx}^2) + b,$$  \hspace{1cm} (1)

where $A_0$ is the NMR intensity when no ultrasonic wave exists, $a$ and $b$ constants satisfying $a + b = 1$, $k$ a constant and $E_{xx}$ the strain amplitude. The constant $b$ was added because, in some part of the crystal where random electric field gradients are produced by lattice imperfections, the acoustic waves can scarcely induce transitions.

The constant $k$ can be calculated easily, and for nuclei of spin $3/2$ it is given by

$$k = (3/160)(eQ/\hbar)^2S_{11}^2T_1g(\nu_c),$$  \hspace{1cm} (2)

where $Q$ is the nuclear quadrupole moment, $T_1$ the spin-lattice relaxation time, and $g(\nu_c)$ the value of the normalized shape function of the acoustic transition at the acoustic frequency.

Because in our experimental condition the strain is not uniform over the sample, the average of (1) should be taken. Assuming a parabolic form for the radial distribution of the strain with the maximum
Gradient-elastic Tensor

value $E_o$ at the axis of the cylinder, the average of (1) was calculated to be

$$\langle A/A_0 \rangle = (a/2E_o\sqrt{k})\log\{2E_o\sqrt{k} + \sqrt{1 + 4kE_o^2} \} + b.$$  \hspace{1cm} (3)

The observed intensity of the NMR signal was found to follow equation (3) as a function of the strain and the constant $k$ was determined.

Using $T_1$ and $g(\nu_o)$ determined by independent measurements, $|S_{11}|$ was calculated by equation (2) and are shown in Table 1.

**Results and discussion.**

$|S_{11}|$ for bromine nucleus shows a minimum at NaBr. By point charge model $|S_{11}|$ for Br is expected to be larger for lighter alkali bromides, being in contradiction to the experimental results. It has been already shown that the overlap of ion cores should be taken into consideration to interpret $T_1$ and the chemical shift in NMR of alkali halides\(^5\). The overlap of ion cores together with the point charge effect give the following $S_{11}$ in the case of NaCl type crystal.

$$S_{11} = \pm 11.8e(1 + \gamma)/a^3 + (8e/5)^{\langle 1/r^3 \rangle} [aD_1/j_1 + (a/\sqrt{2}j_2 - 3)D_2]$$ \hspace{1cm} (4)

where $a$ is the interionic distance, $\gamma$ the antishielding factor, $\langle 1/r^3 \rangle$ the average of $1/r^3$ over the p-orbital, $D_1/2$ and $D_2/2$ the squares of the total overlap integrals with the nearest and next to the nearest neighbors, respectively\(^6\). $D_1$ and $D_2$ are assumed to vary exponentially with the interionic distance and $1/j_1$ and $1/j_2$ are constants in the exponents for $D_1$ and $D_2$, respectively. $D_1$, $D_2$, $j_1$ and $j_2$ were calculated numerically by the overlap integrals given by Hafemeister and Flygare\(^7\). In (4), the sign + is for alkali and - for bromine nucleus.

The calculated values of $S_{11}$ by (4) using appropriate values of $\gamma$ and $\langle 1/r^3 \rangle$ are shown in Table 1. Though there remains uncertainty due to the inaccuracy of numerical values of these constants, the agreement between $|S_{11}|_{\text{exp}}$ and $|S_{11},\text{cal}|$ seems satisfactory, suggesting that the overlap of ion cores has an important contribution to
Gradient-elastic Tensor

$S_{11}$ in addition to the point charge effect.

| sample  | nucleus | $|S_{11}|_{\text{exp}}$ \(10^{-15} \text{ statC/cm}^3\) | $S_{11}$, cal \(\%\) |
|---------|---------|-------------------------------------------------|------------------|
| LiBr    | Br$^{79}$ | 13−30                                           | −9.4             |
| NaBr    | Br$^{79}$ | 3.6                                             | −5.0             |
| KBr     | Br$^{79}$ | 4.6                                             | +5.6             |
| RbBr    | Br$^{79}$ | 7.5                                             | +10.2            |
| CsBr    | Br$^{79}$ | 16                                              | +15.8            |
| LiBr    | Li$^7$   | 1.5−3.5                                         | +0.47            |
| NaBr    | Na$^{23}$ | 2.3                                             | +2.4             |
| KBr     | K$^{39}$  | −                                                | +6.8             |
| RbBr    | Rb$^{87}$ | 8.0                                             | +11.8            |
| CsBr    | Cs$^{133}$ | 9−73                                            | −10.1            |

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Double-Quantum Versus Piezoelectric Detection of Microwave Phonons

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Introduction

In this paper the acoustic attenuation measured by piezoelectric detection of microwave phonons is compared with that measured by double-quantum detection. The envelope of microwave phonon echoes generated and detected by the piezoelectric effect is generally ragged, with maxima and minima (Fig. 1, bottom), caused by phase-averaging or interference effects that arise from nonparallelism of the sample endfaces and misalignment of the crystalline axes. It is, however, possible to roughly fit an exponential to the echo envelope, and this has been a common method of estimating acoustic attenuation. An exponential decay is observed in double-quantum detection by phonon-photon transitions in paramagnetic Fe$^{2+}$ ions.
Double-Quantum Versus Piezoelectric Detection of Microwave Phonons

in MgO (Fig. 1, top). We have compared the attenuation measured by the two methods in the same MgO sample for phonon frequencies of 3.1-, 4.7-, and 9.3-GHz. Andrews and Strandberg attempted to measure the absolute attenuation of 9-GHz phonons by using a superconducting bolometer on one end of an X-cut quartz sample; since most of the acoustic energy was lost in the bolometer, however, it was not possible to measure the intrinsic loss in the quartz. The double-quantum method used in the present experiment measures the intrinsic acoustic loss in the MgO.

Experimental Method

Longitudinal microwave phonons were generated with a CdS transducer deposited on the end of a (100)-oriented rod placed in a coaxial type of reentrant cavity that was excited by 0.5-µsec pulses from the magnetron (Fig. 2). The cavity was tuned with a movable dielectric disk to resonate in overtone modes at about 3.1-, 4.7-, and 9.3-GHz. When the phonon pulse returned to the transducer, it was detected with a superheterodyne receiver. The double-quantum detection took place when the phonon pulse was inside the sapphire-filled \( TE_{012} \) rectangular cavity resonant at 8.7 GHz. The phonon-photon double-quantum transition, which took place at a magnetic field where the separation of the energy levels in \( Fe^{2+} \) corresponded to the sum of the phonon and photon frequencies, caused photon power from the X-band frequency-stabilized source to be absorbed. The change in absorption was detected with a 1N23G crystal diode, amplified, and displayed on an oscilloscope. The echoes shown in Fig. 1 for Sample Number 1 were observed with the end of the rod completely inside the sapphire-filled cavity. The experiment was performed at 1.5°K.
Double-Quantum Versus Piezoelectric Detection of Microwave Phonons

Discussion of Results

The experimental attenuation measurements are summarized in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency (GHz)</th>
<th>Attenuation (dB/cm)</th>
<th>Piezoelectric</th>
<th>Double-Quantum</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.1</td>
<td>0.4 ± 0.2</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td>2.3 ± 2</td>
<td>1.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>3 ± 1</td>
<td>2.2 ± 0.3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>2.6 ± 1</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td>2.5 ± 1.5</td>
<td>2.3 ± 0.5</td>
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<td></td>
<td>9</td>
<td>4.4 ± 2</td>
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<tr>
<td>3</td>
<td>4.7</td>
<td>2.5 ± 1</td>
<td>2.1</td>
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<td></td>
<td>9</td>
<td>1.5 ± 1</td>
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<td>2.7 ± 1</td>
<td>1.4</td>
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</tr>
<tr>
<td></td>
<td>9</td>
<td>2.7 ± 1</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

The large spread in the attenuation measured by piezoelectric detection is due to the uncertainty in fitting the observed echoes to an exponential. The uncertainty for the 3.1-GHz phonons shown in Fig. 1 became less at 9 GHz, where the phonon attenuation was greater and the piezoelectrically detected echo envelope more nearly exponential. The experimental uncertainty was within 10% for the double-quantum attenuation data taken in a given run. The greater uncertainty in the table was observed from one run to the next. Between runs the rod was warmed up to room temperature and removed from the experimental cavities. Where there is no tabulated uncertainty, there was only one run made. The change in attenuation from run to run followed no set pattern. On some successive runs it increased whereas on others it decreased. Dislocation motion due to the thermal gradients in cycling the sample from 300 K to 1.5 K and changes in the mounting stress are the most likely causes.

The frequency-dependence of the attenuation gives an indication of the scattering mechanism. Scattering from external boundaries of the sample and from grain boundaries shows no frequency-dependence whereas scattering from strain-field dislocations shows an attenuation proportional to the frequency. Since the observed attenuation is at the most proportional to the frequency, the scattering is from
Double-Quantum Versus Piezoelectric Detection of Microwave Phonons

boundaries and dislocations. The frequency dependence is too small for the attenuation to be due to the absorption of phonon energy by $\Delta M = 1$ spin-phonon transitions between energy levels whose spacing corresponds to the phonon frequency. Additional confirmation comes from a comparison of the attenuation of 9.3-GHz phonons measured by piezoelectric detection at a double-quantum field of 1.9 kG (where this mechanism should be the largest) with that measured at zero magnetic field (where it should be negligible). Individual echoes increase or decrease similarly as in Fig. 1, but there is no observable change in the attenuation. The method of estimating the attenuation by fitting an exponential to the piezoelectrically detected echoes comes within a factor of about 2 of being equal to the absolute attenuation as measured by double-quantum detection.

We wish to thank M.R. Stiglitz for designing the cavities, Dr.J. deKlerk for fabricating the CdS transducers, and TSgt J.H. Silva for technical assistance.

References
Conversion of Acoustic Energy to Phonon Energy in Metals

Warren P. Mason
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Introduction - Dielectric Crystals

In dielectric crystals without imperfection motions - such as dislocations, domain walls, etc. - it has been established that the cause of acoustic attenuation is the direct conversion of acoustic energy into phonon energy. This occurs through two mechanisms, the thermoelastic effect and the Akheiser effect. The thermoelastic loss is small and accounts for less than 4 percent of the total loss. The Akheiser loss - which represents a loss associated with a sudden separation of the temperatures of the longitudinal and shear phonon modes, followed by their equilibrium in the thermal relaxation time $\tau$ - is the principal source of loss in dielectric crystals. It has been shown that the separation in temperatures of the phonon modes is associated with the values of the third order - non-linear elastic moduli - and calculations for 6 cubic crystals give results within less than a factor of two with the measured results. Calculations for the trigonal crystal quartz has recently been completed by M. F. Lewis (General Electric Co. Ltd of England) and again the results are within a factor of two with
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respect to the measured results.

Sources of Loss in Metal Crystals

In metals the thermoelastic effect is larger on account of the increased thermal conductivity due to electrons and this source provides about 1/3 to 1/2 of the total loss. The Akheiser effect is still important but its formulation has to be modified since the equilibrium of the phonon modes occurs through the lattice thermal conductivity rather than through the electronic thermal conductivity. The lattice thermal conductivity for copper has been directly measured (White and Wood, Phil. Mag. 45, 1343, 1954) by measuring the thermal conductivity of two copper samples with different amounts of impurities. For other cubic crystals the lattice thermal conductivity can be estimated from a theoretical model due to Leibfried and Schloemann. Third-order elastic moduli have been measured for copper (Hiki and Granato, Phys. Rev., 144, 411, 1966).

Measurements for Copper

In order to compare the calculated Akheiser loss with experimental results, attenuation measurements have been made for copper for the longitudinal and the shear waves over a temperature range. The dislocation and square law losses can be separated by using standard curves. The square law attenuation for longitudinal waves can be accounted for by three mechanisms, the thermoelastic effect, the phonon viscosity effect and the damping due to interactions of phonons with electrons. At room temperature the phonon viscosity effect is slightly larger than the thermoelastic effect and indicates a non-linearity constant D = 42.8. Calculations using the third-order moduli of Granato and Hiki give good agreement with this value. At low temperatures the electronic loss
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prevails and prevents an evaluation of the thermoelastic loss and Akheiser loss below about 77°K. The electronic loss is in good agreement with that calculated from the free electron model.

Measurement for Cadmium

Recently measurements have been made of the attenuation of longitudinal waves along and perpendicular to the c axis of cadmium. All the free dislocations in cadmium lie in a plane perpendicular to the c axis and these are not actuated by the two types of longitudinal waves or by shear waves along an axis perpendicular to c with the polarization of the shear waves along the c axis. Hence for these three waves, there is no dislocation loss and all the loss varies as the square of the frequency. By correcting for spreading and transducer loss good square law curves are obtained.

The results for this hexagonal crystal are interesting since they indicate a large non-linear constant $D_{\parallel c}$ and a small constant for longitudinal waves perpendicular to c. The lattice thermal conductivity is approximated by subtracting the electronic thermal conductivity from the total measured thermal conductivity. With these values the non-linear constant $D_{\parallel c} = 58$ and $D_{\perp c} = 8.85$. For longitudinal waves along the c axis the Akheiser loss is about twice the thermoelastic loss while for a longitudinal wave perpendicular to c the Akheiser loss is about 50 percent of the thermoelastic loss. While no third-order moduli have been measured for cadmium, the average of the three directions is less than that for copper.

Conclusions

It appears that present measurements indicate that the attenuation of acoustic waves in metals is associated with the three mechanisms,
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 thermoelastic loss, Akheiser type loss and phonon electron losses. The Akheiser loss agrees reasonably well with that calculated from third-order elastic moduli.

Fig. 1 Square law attenuation for copper, measured at 150 MHz, for a longitudinal wave along <100>.
Recently, propagation of N-shaped shock pulses in air has been investigated by various types of source.\(^1\)\(^2\) It has been obtained that the propagation velocity of shock pulses is not identical with those of infinitesimal sound waves and increment of velocity is proportional to excess peak pressure. For the attenuation of shock pulses, it has been found theoretically to be proportional to ratio of the excess peak pressure to width of N-shape.\(^1\) In the present paper, it is concerned that the attenuation of shock pulses propagating in circular pipe is measured and is discussed theoretically. The measurements were made in a circular pipe with 57 mm in inner diameter and 3 meters in length. An example of the formation of N-shaped shock pulses is shown in Fig. 1. It is found that the N-shaped form is performed at the point of about one meter from the source and thereafter the width of N-shape increases with propagation in the pipe. The experiments are made by a source of electro-magnetic induction type developed by Eisenmenger.\(^3\)\(^4\)\(^5\)\(^6\) In Fig. 2, the pulse form on the cross section of the pipe at 280 cm from the source are shown. All wave forms in this figure are identical, and then one may be considered that the wave front propagates like plane wave in this pipe. This condition was
established at a distance of about one meter from the source.

The finite amplitude shock pulses propagating in medium tend
to increase the pulse width and decrease the peak pressure according
to following equation. \(^1\)

\[
-\frac{1}{S} \frac{dS}{d\chi} = \left( \frac{\gamma + 1}{2\gamma} \right) \frac{S}{L} \tag{1}
\]

and

\[
\frac{1}{L} \frac{dL}{d\chi} = \left( \frac{\gamma + 1}{2\gamma} \right) \frac{S}{L} \tag{2}
\]

where \(S\) and \(L\) are excess pressure ratio and width of \(N\)-shape,
respectively, and \(\gamma\) is specific heat ratio of air. If \(P_1\) and \(P_0\)
are peak pressure and equilibrium pressure, respectively, \(S\) is
equal to \((P_1 - P_0)/P_0\). In

Fig. 3, the results obtained
for rate of increment of the
pulse width and the attenua-
tion of the peak pressure
are shown. The rate of the
increment of the pulse width
agrees with Eq. (2), as
shown in Fig. 3. The attenua-
tion of \(S\) are corrected
with the friction effect on
the tube wall, and then the
proportional constant is
\((\gamma + 1)/2\gamma^3\).

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For the finite amplitude sound waves, the wave length is held a constant value and the attenuation constant, \( \alpha \), is represented by following expression,

\[
\alpha = 2 \left( \frac{Y+1}{2Y} \right) \frac{\delta}{\lambda},
\]

where \( \lambda \) is wave length and \( \delta \) is ratio of the pressure amplitude to the equilibrium pressure. This is twice as large as the attenuation obtained from Eq. (1). If one may consider an attenuation of \( \delta/L \) for the sound pulses, it may agree with an attenuation of \( \delta/\lambda \) for the sound waves as following, that is, for the sound pulses

\[
- \frac{1}{\left( \frac{\delta}{L} \right)} \frac{d}{dx} \left( \frac{\delta}{L} \right) = - \frac{1}{\delta} \frac{d\delta}{dx} + \frac{1}{L} \frac{dL}{dx} = 2 \left( \frac{Y+1}{2Y} \right) \frac{\delta}{L},
\]

and for the sound waves

\[
- \frac{1}{\left( \frac{\delta}{\lambda} \right)} \frac{d}{dx} \left( \frac{\delta}{\lambda} \right) = - \frac{1}{\delta} \frac{d\delta}{dx} = 2 \left( \frac{Y+1}{2Y} \right) \frac{\delta}{\lambda}.
\]

The observed values of \( \delta/L \) are shown in Fig. 4 as a function of the relative distance. Each observed values for the pulses of the different intensity may be plotted by displacing it along the x-axis until these plots coincided with a curve. Then, tangents to the smooth curve are used to obtain the attenuation constants of \( \delta/L \) at various intensities. The results obtained are shown in Fig. 5. If one correct observed values with the attenuation by the friction effect, the attenuation of \( \delta/L \) is proportional to \( \delta/L \) and a proportional constant is equal to \( 2(Y+1)/2Y^2 \). On the other hand, the experiments for the sound waves give \( 2(Y+1)/2Y^2 \) for the proportional constant. Then, it may be found that both attenuations of \( \delta/L \) for the sound pulses and \( \delta/\lambda \) for the sound waves

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coincide experimentally.

References
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Fig. 5
Measurement of the Snoek Peak by
Ultrasonic Lamb Waves.
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Central Research Laboratories,
Fuji Iron & Steel Co., Ltd.

Introduction
An extraordinary attenuation of ultrasonic Lamb waves in mild steel sheets at high temperature was observed. We studied the phenomenon qualitatively and confirmed that it is due to the Snoek damping of carbon and nitrogen dissolved in the steel. Other studies of the Snoek damping of ultrasonic longitudinal wave in steel were also reported at about the same time.

Experimental apparatus and specimens
An ultrasonic flaw detector of the type Sperry UR-1C and a 2.25 MHz variable angle probe with a quartz transducer were used. The heating apparatus used is shown in Fig. 1. The chemical composition and the thickness of the specimens are shown in Table 1.

Preliminary experiment
A preliminary experiment was necessary to devise a method to get attenuation constants of Lamb waves transmitting in a specimen having a temperature gradient in the longitudinal direction. As shown in Fig. 1, a hole was drilled through the specimen. When the temperature is uniform throughout the specimen, the amplitudes of end echo and reflection echo from the hole P and P_{ef} are expressed as follows:

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Measurement of Snoek peak by ultrasonic Lamb waves

Table 1. Chemical composition of specimens.

<table>
<thead>
<tr>
<th>No.</th>
<th>Classification of Specimens</th>
<th>Thickness (mm)</th>
<th>Chemical Composition (%)</th>
<th>Sol. C (%)</th>
<th>Sol. N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cold rolled rimmed sheet</td>
<td>1.0</td>
<td>0.0465 0.28 0.015 0.024</td>
<td>0.0023</td>
<td>0.013-23</td>
</tr>
<tr>
<td>2</td>
<td>Hot rolled rimmed sheet</td>
<td>1.9</td>
<td>0.0395 0.25 0.015 0.021</td>
<td>0.0028</td>
<td>0.013-23</td>
</tr>
<tr>
<td>3</td>
<td>rimmed sheet</td>
<td>2.3</td>
<td>0.086 0.52 0.015 0.033</td>
<td>0.050</td>
<td>0.013-23</td>
</tr>
<tr>
<td>4</td>
<td>Cold rolled rimmed sheet</td>
<td>3.1</td>
<td>0.021 0.19 0.009 0.022</td>
<td>0.0028</td>
<td>0.013-23</td>
</tr>
<tr>
<td>5</td>
<td>Al-killed sheet</td>
<td>2.0</td>
<td>0.0326 0.32 0.015 0.032</td>
<td>0.0048 0.033</td>
<td>0.0012-17</td>
</tr>
<tr>
<td>6</td>
<td>Al-killed rimmed sheet</td>
<td>2.3</td>
<td>0.0455 0.36 0.015 0.011</td>
<td>0.0053 0.10</td>
<td>0.0012-17</td>
</tr>
<tr>
<td>7</td>
<td>Decarburized rimmed sheet</td>
<td>1.0</td>
<td>0.0030 0.30 0.007 0.009</td>
<td>0.0011</td>
<td>0.00024-50</td>
</tr>
</tbody>
</table>

\[
P = P_0 e^{-ar} \frac{1}{\sqrt{r}} \quad \text{---- (1)}
\]

\[
P_{def} = R P_0 e^{-ar} \frac{1}{\sqrt{r}} \quad \text{---- (2)}
\]

where \( R \) is the reflection ratio of Lamb waves at the hole, \( r \) is the round trip distance from the probe to the end or hole of the specimen, and \( P_0 \) is the end echo amplitude when \( a = 0, \ r = 1 \). When there is a temperature gradient in specimen between the probe and the hole, and the temperature is uniform from the hole to the end, the two echo amplitudes may be expressed as follows:

\[
P = P_0 \exp \left( -2 \int_0^L a' dr - 2a (L - \ell) \right) \times \frac{1}{\sqrt{2L}} \quad \text{---- (3)}
\]

\[
P_{def} = R P_0 \exp \left( -2 \int_0^L a' dr \right) \times \frac{1}{\sqrt{2L}} \quad \text{---- (4)}
\]

where \( a' \) is the attenuation of the part of the sheet between the probe and the hole, \( a \) is that between the hole and the end of the sheet inside the furnace and \( R \) is assumed to be constant. Thus, \( a \) is constant at the specified temperature and \( a' \) is a function of \( r \). From Eq. 3 and Eq. 4 \( a \) is derived in the next equation:

\[
a (dB) = \left( -20 \log R + 10 \log (L/\ell) \right) + 20 \log \frac{P_{def}}{P} + 2(L-\ell) \quad \text{---- (5)}
\]

This equation was confirmed by measuring \( 20 \log P_{def}/P \) for several specimens which have different \( \ell \) and drilled holes at temperatures up to 500°C.

Theory

The Snoek peak temperature \( T \) at which the internal friction \( Q^{-1} \)
Measurement of Snoek peak by ultrasonic Lamb waves

reach maximum value $Q^{-1\text{ max}}$ is given by the following equation:

$$T = \frac{0.434 A}{R} \times \frac{1}{\log(36 D_0 / \alpha \omega)}$$  \hspace{1cm} ----- (6)

Using the values of $A$ and $D_0$ for iron derived by Lord et al., the Snoek peak temperature of nitrogen $T_N$ and carbon $T_c$ at 2.25 MHz are calculated; $T_N = 286^\circ\text{C}$ and $T_c = 317^\circ\text{C}$.

The internal friction $Q^{-1}$ is given by the following equation:

$$Q^{-1} = \alpha v / \pi f \quad \quad (\alpha \text{ in neper}) \quad \quad ----- (7)$$

and the $Q^{-1}$ is calculated as follows in this experiment:

$$Q^{-1} = 1.63 \times 10^{-8} \times \angle\alpha \cdot \nu \quad \quad (\alpha \text{ in dB/m}) \quad \quad ----- (8)$$

where group velocity in m/sec is used as $\nu$.

The relation between $Q^{-1\text{ max}}$ and the amount of solute carbon, $C$, or nitrogen, $N$, in steel is expressed as follows:

$$N = Q^{-1\text{ max}} \cdot T / 220 \quad \quad ----- (9)$$

$$C = Q^{-1\text{ max}} \cdot T / 270 \quad \quad ----- (10)$$

Where $T$ is the absolute peak temperature.

Experimental results

All the rimmed steel specimens except the decarburized one showed a clear high peak of $\alpha$ or $Q^{-1}$ at around $T_N$ like Fig. 2. Although the aluminium killed steel specimens showed the $\alpha$ or the $Q^{-1}$ peak at around $T_c$, the peak is neither clear nor high. We have used group velocity in Eq. 8 for two reasons: first, the difference of $Q^{-1}$ among modes is much greater when phase velocity is used, and second, the maximum value of $\angle\alpha$ is inversely proportional to $\nu$ when the group velocity is used, satisfying Eq. 8.

The experimental

---fig 2---

Effect of temperature on Lamb wave attenuation and internal friction. (1.9 mm rimmed sheet)

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results for solute carbon and nitrogen concentration approximately satisfied Eq. 9 and Eq. 10.

The aging index of specimens were measured by a tensile testing machine having a constant crosshead speed. The relation between the aging index and $Q^{-1} \text{max}$ of the specimens is shown in Fig. 3. The result is similar to that reported before.

The decrease of end echo amplitude $\Delta P$ in dB from room temperature to the Snoek peak temperature and the increase of the attenuation $\Delta \alpha$ between the same temperature for all the specimens were measured and was found to be expressed as follows under the experimental conditions:

$$\Delta \alpha = 0.68 \Delta P$$  \hspace{1cm} (11)

Lastly, phenomenon which was inferred to be due to the solution of precipitated carbon or nitrogen atoms at high temperature was observed by repeating the heating and cooling the specimens.

Conclusions
1. A suitable method of measuring ultrasonic Lamb wave attenuation at high temperature has been established.
2. The $Q^{-1} \text{max}$ values by pulsed Lamb waves at 2.25 MHz for steel were roughly equal to the double of the concentration of solute carbon and nitrogen atoms in the specimens, following the Smit's relation.
3. Group velocity is found to be suitable for the velocity of waves to obtain $Q^{-1}$.
4. The relation between the aging index and $Q^{-1} \text{max}$ of specimens is found to be quite similar to that reported before.
5. The solution of precipitated atoms, carbon and or nitrogen, is observed when the specimen is heated above 325 °C.
Structure Changes in Metal Fatigued
at an Ultrasonic Frequency

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Introduction

Fatigue of metal at high frequencies is now presenting some
knotty problems in the strength of parts of the aircraft and other
high speed machines. By the recent studies on this subject, frequency
dependence of fatigue character has been clarified and it has thrown
light on a clue for solving the fatigue mechanism. To investigate more
in detail, the present author and his associates studied by a light
microscope the surface behavior resulted from the fatigue. Now, we
are in the position to state the structure changes induced in the
specimens fatigued at ultrasonic frequencies.

Specimens and Experiments

As the fatigue character at ultrasonic
frequencies was expected to be affected by
vacancies, pure aluminium was used for tests.
Because this material has been well studied
on the behaviors of vacancies in it. A test
piece fixed at the top of the testing machine
(Fig.1) was made by drawing several times the
rod 6 mm in diameter to 3 mm in diameter,
excepting one end of the rod. These were
Structure Changes in Fatigued Specimens

Fig. 2 Structure in the drawing Al. Fig. 3 Structure in the annealed Al. used after annealing at 235°C for 3hrs. Structure changes from drawing to annealing are seen by comparing Fig. 2 and Fig. 3, the surface structure revealed by etching is shown by Fig. 4. S-N curve (Fig. 5) was obtained by tests at a frequency 17.7 kc/s, cooling the test pieces by a continuous flow of water (11°C, 2 L/min). The amplitude of stress has sinusoidal distribution along the length of test piece and the maximum value in its middle. Then the specimens for the electron microscope were prepared from the part above 95% of the maximum value of stress. At first, disks of thickness about 0.2 mm were strain-freely cut from this part by the electrolytic slitting wheel made by the author. And then, the jet technique was adopted to make a cavity in the center of the disk. Finally, an electropolishing apparatus equipped with a light source was used to make a very small hole in the cavity, the periphery
Structure Changes in Fatigued Specimens

Fig. 6 Dislocation patch
Fig. 7 Dislocation patch
of the hole being an electron transmission area, about 5000Å in thickness. The electron microscope adopted here was Hitach HU-11 type operated at 100KV.

Observations and Results.

Various dislocation arrangements were observed, similar to those in specimens fatigued at the ordinary frequencies (50 c/s or so). One of these is the so-called dislocation patch. Some of them are shown in Fig. 6 and Fig. 7, the former being composed by the comparatively low dislocation density and the latter by the high dislocation density. The layer-like patch was also observed. In these micrographs, however, dislocation loops are abundantly seen besides the patch, these being likely to result from the condensation of vacancies. These loops are very rarely observed in the or-

Fig. 8 Cell-structure
Fig. 9 Cell-structure

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Structure Changes in Fatigued Specimens

Fig. 10 Dislocation loops

Fig. 11 Jogs

dinary fatigued-specimens.

Fig. 8 and Fig. 9 show the cell structures; micro-cracks being presumed to take preferentially the route along its boundary. Weismann et al who found the similar structure to that in Fig. 9 in the ordinary fatigued-specimen, called it birds-nests and regarded as a precursor of micro-cracks. A lot of loops are also seen in these figures. Fig. 10 shows the region in which the loops are clear seen. It is ambiguous whether these resulted from the vacancy-condensation or from the dislocation dipole. Both types of loop are expected to exist there, because a few loops with the stacking fault can be observed in them. Fig. 11 shows the jog, the source of vacancies (A), and the large jogs, from which the dislocation dipoles are formed, (B), (C) and (D).

Fig. 12 shows voids presumably formed by the condensation of vacancies, being similar to those observed sometimes in quenching. (Temperature rising of the tests pieces in tests is very little to measure by the thermo-crayon which discolors at 40°C).

Besides these, some other unexpected structures were observed; these will be shown at the meeting.

Fig. 12 Voids
Introduction

The experimental evidence is very convincing that seismic waves experience an exponential attenuation in which the coefficient varies as the first power of frequency. Stated another way, earth materials are characterized by a loss parameter Q which is independent of frequency. Several nonlinear stress-strain relations have been proposed in the literature, each of which would agree with the above experiments. The stress-strain relation to be discussed here can be related to static friction and sliding friction at areas of contact between grains, for a loose granular material. In this paper, the relation should be taken as a pure assumption, whose worth rests on the resulting properties of the medium under vibration and stress.

Stress-Strain Relation

In an elastic medium, stress $\sigma$ equals the product of strain $\varepsilon$ and an elastic constant $K$. The heavy line at $45^\circ$ in Fig. 1 denotes this

Fig. 1. Diagram Relating Strain to Applied Stress Transient

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Strains in a "Constant Q" Solid

relation. An assumed stress transient is shown in the upper left part of Fig. 1. For the nonlinear medium, stress increases from zero along the line $\sigma = K(1+\gamma)\varepsilon$, where $\gamma$ is a small dimensionless loss parameter. Stress drops to the elastic line before strain begins to decrease, then follows a line whose slope is also $K(1+\gamma)$. At the minimum, stress increases to the elastic line before strain starts to increase. The resulting strain transient is also shown in Fig. 1, with flat spots at the extrema. This relation was programmed so that the strain could be computed due to any assumed stress.

Phase Angle Between Stress and Strain

If stress is $P \sin \omega t$, then strain is approximately $P \sin (\omega t - 4\gamma/\pi)$. The computed strain agreed with this result, yielding a phase angle of $0.0124$ for $\gamma=0.01$, or $4\gamma/\pi=0.0128$. All harmonics were down by a factor of $10^4$ or more. To see how well superposition applies in this slightly nonlinear solid, a stress transient was chosen which consists of harmonics 5 through 15 at equal amplitudes. The computed strain wave form is shown in Fig. 2, consisting of harmonics 5 through 15, of very nearly unit amplitude, and phase angles given in Table I. These don't differ drastically from 0.0128. Harmonic 16 was down by a factor of 300, and higher harmonics were much smaller.

![Strain Wave Form](image)

**Table I. Stress-Strain Phase Angles**

<table>
<thead>
<tr>
<th>Harmonic</th>
<th>Phase Angle in Radians</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.0145</td>
</tr>
<tr>
<td>6</td>
<td>0.0143</td>
</tr>
<tr>
<td>7</td>
<td>0.0137</td>
</tr>
<tr>
<td>8</td>
<td>0.0149</td>
</tr>
<tr>
<td>9</td>
<td>0.0150</td>
</tr>
<tr>
<td>10</td>
<td>0.0161</td>
</tr>
<tr>
<td>11</td>
<td>0.0141</td>
</tr>
<tr>
<td>12</td>
<td>0.0129</td>
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<tr>
<td>13</td>
<td>0.0124</td>
</tr>
<tr>
<td>14</td>
<td>0.0116</td>
</tr>
<tr>
<td>15</td>
<td>0.0103</td>
</tr>
</tbody>
</table>
Strains in a "Constant Q" Solid

Effect of Initial Stress

Another feature of this nonlinear model is shown in Fig. 3. In this case, $\gamma$ has the abnormally large value of 0.1. In the left plot, there is no initial stress or strain, and the curve returns to the starting-point as the stress oscillates with decreasing amplitude. On the right, a monotonically increasing prestress of 2.0 units has created an initial strain of 1.8 units, approximately. As the oscillating stress dies down now, strain approaches 2.0 units, which lies on the elastic line referred to earlier. Thus an oscillating stress has been responsible for a permanent strain, in this prestressed medium.

Simulated Earth Tides

In Fig. 4, the prestressed condition is pictured as being due to the earth tide, with shifts in strain occurring with the passage of an "earthquake". These curves show computed strains in an elementary volume of the nonlinear medium when the stress consists of a damped oscillation superimposed on a long-period sinusoid. Parameter $\gamma$ is again 0.1. Due to this mechanism the strain shift must always be a small fraction of the peak tidal strain.

Fig. 3. Two Stress-Strain Histories Due to the Same Applied Stress Transient
Conclusions

Fourier analysis of computed strain has shown that for sinusoidal applied stress, the small nonlinearity causes a phase shift between stress and strain, with little harmonic distortion. The same applies to each frequency component of a pulse, indicating that superposition is approximately satisfied. When a large prestress exists, vibration may cause a shift in strain which is appreciable, even though small compared to the prestress.
About a new mechanic-electric effect

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Exposition

A new physical effect was recognized as follows. The surface of a plate of microcrystalline structure material being neither a real isolator nor a typical semiconductor is plane polished. A similarly plane polished well conducting metal plate is put over it. To the other surface of the semiconductor an electrode is stucked or evaporated and the potential difference between the two electrodes is measured by an electronic voltmeter. In static condition the system does not show any potential difference. Now a force perpendicular to the surfaces of contact is exerted. When pressing, potential difference occurs between the surfaces which slowly comes to an end after discharging the system. When pressing, the current is directed from the semiconductor to the metal plate. After discontinuing the pressure a voltage of opposite sign can be measured which in a short time also diminishes to zero. The value of the originated potential depends on the size of the surface, on the exerted force, on the finish of surfaces, further on temperature and on relative humidity.

A scheme of the experiment is shown in Fig.1. For the time being the experiments have been carried out with a few materials and at room temperature only. The physical data of a sample material producing relatively maximum effect are to be seen in Table I. The finish of surface has an accuracy of about $2\ldots3\mu$. For this reason there is a layer of air interrupted by bridges between the contiguous surfaces which represents a considerable capacity. The resistance of the bridges is far higher than that of the material. The ratio is about
About a new mechanic-electric effect

200...1000 which extremely depends on the relative humidity of air. In dry air some minutes after touching together in static condition no contact potential can be measured at all.

Table I.

<table>
<thead>
<tr>
<th>Physical data of the material used for experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific weight</td>
</tr>
<tr>
<td>Modulus of elast.</td>
</tr>
<tr>
<td>Specific resist.</td>
</tr>
<tr>
<td>Temperature coeff.</td>
</tr>
<tr>
<td>Dielectric const.</td>
</tr>
</tbody>
</table>

Fig.1. The scheme of the system

Experiments

When the contact system of 10 cm² is loaded by a force of 1 kp or when this loading is ceased the occurring potential will be ~10 mV. If external voltage is put between the metal plate and the counter electrode the effect will suddenly increase. When e.g. putting the system under an external voltage of 10 V the effect will increase 20-times, when taking a voltage of 240 V the value of the effect increases 500-times. The direction of the "cold effect" remains unchanged if negative potential is connected to the metal plate. In the reversed case the direction of the effect will change. In this latter case - at a certain value of the external voltage - the effect may be completely put out. When taking the former data (10 cm², 1 kp) this value is 0.2...0.5 V. Thus, the layer between the contiguous surfaces may be considered at small voltages as a rectifier with barrier layer.

The effect is not a piezoelectric one. If to both sides of the semiconductor electrodes are evaporated, the effect disappears. So, only the physical processes occurring between the contiguous polished surfaces are responsible for the effect. The explanation by Volta contact potential is also to be rejected, as in static condition no generated potential can be traced in the system.

The new effect is similar to the reciprocal process of the so called Johnsen-Rahbek effect, discovered in 1917. This is being the adhesion experienced between a metal plate and a semiconductor plate, polished together, when putting on voltage. The two effects, however, are not completely reciprocal. First, the Johnsen-Rahbek phenomenon does not include the cold effect being to our opinion of essential importance. Another difference is that the Johnsen-Rahbek effect is
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first of all a static phenomenon, due to the inertia of discharge. The effect discovered now, on the contrary, can just be maintained if the mechanical generation is being periodical, consequently the phenomenon is above all dynamical. The inertia of the discharge displays itself in the diminishing of the effect in the direction of high frequencies.

Fig. 2. a) and b) schema of experiments; c) substitutional circuit

A group of experiments consisted in the investigation of this dynamic effect. The system was excited in two ways as shown in Fig.2. In the first series periodical pressure was exerted on the system lying on a stiff ground, in the second one the system was placed on a Brüel & Kjaer Type 4290 calibration exciter. In both cases the feedback principle was used in order to have a mechanical excitation resulting in an acceleration independent of frequency. A schematic diagram in Fig.2 c) shows the substitutional circuit of the experiments.

Fig.3. Recorded frequency diagrams 1) of B & K 4332 accelerometer and 2) of the new effect (surface 50 cm²; bias voltage +4.5 V)
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For comparison an accelerometer of Bruel & Kjaer Type 4332 was used. In Fig. 3, typical recorded diagrams are shown. The frequency function of the excitation with feedback was registrated by means of the accelerometer and by help of the new effect with a surface of 50 cm². This time the bias voltage was +4,5 V in order to get the same sensitivity with the receiver used for checking which was 50 mV/G.

It is to be mentioned that the small sensitivity of the new effect may be augmented partly by increasing the surface and partly by increasing the bias voltage. The same sensitivity than that of the accelerometer used for checking can be attained by an 11 cm² plate at a bias voltage of +10 V or by an about 1 cm² plate at a bias voltage of +200 V. Moreover the finish of surface and quality of material also play part in the magnitude of the effect. Maybe that in the future more sensitive systems can be constructed too.

Explanation

The physical explanation of the effect is only in its initial stage. In static condition the Fermi levels in the contact points - the bridges - take up the same height. In these places in the state of equilibrium, the energy level of the conducting band of semiconductor will rise. Between the surfaces having, however, an extremely small distance (0,5...2μ) some field intensity develops. When pressing the plates, a distortion occurs in the structure of the static energy bands, at the same time the number of bridges increases and till the state of equilibrium is reached, electrons flow in the direction of the semiconductor.

If the system is put under external voltage and the metal is negative, the field intensity and consequently the effect increases. If, however, the metal is positive, up to a certain potential value which corresponds to the value of the potential barrier, the effect diminishes to zero. According to the measurements this value is 0,2...0,5 eV. Increasing the voltage the effect appears again but in reversed direction, i.e. due to pressure, passing the forbidden band of semiconductor, electrons enter the metal. An important part is played in the effect by the microcrystalline structure of the semiconductor and the condition created by the polish of individual crystals.
Propagation Constant and Characteristic Impedance of a Plane Longitudinal Wave in the Disperse System of Viscoelastic Materials

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In this paper the propagation constant $\gamma$ and characteristic impedance $Z$ of a plane longitudinal wave propagating in a disperse system composed of an isotropic viscoelastic material and spherical particles of another isotropic viscoelastic material dilutely dispersed in the former are calculated. In what follows the quantities with suffix 1 and 2 are referred to the medium and spheres respectively.

Fundamental formulas

We start with some fundamental formulas which express $\gamma$ and $Z$ of disperse system containing many scatterers in terms of the "amplitude function" of a single scattering particle. Let a particle be placed at a point $O$ in the wave field of a plane scalar wave $(\text{of any kind})$ propagating in the positive z-direction,

$$U_0 = e^{-ik_0z + i\omega t}, \quad z > 0$$

(1)

where $k_0$ denotes the wave number in the medium. The scattered wave at a distant point $P$ from the scattering particle is a spherical, outgoing wave with amplitude inversely proportional to the distance $r$ from the particle. We may therefore write the amplitude of the scattered wave $U_s$ in the form

$$U_s(P) = f(\theta, \phi) \frac{e^{-ik_0r}}{ik_0 r} U_0(O)$$

(2)

thereby defining the "amplitude function" $f(\theta, \phi)$ of the scattering particle. Here $\theta$ and $\phi$ represent the polar and azimuthal angles of $\overrightarrow{OP}$ respectively.

Then the extinction cross section $C_{\text{ext}}$ in the presence of a single particle is given by

$$C_{\text{ext}} = C_{\text{ext},1} + 4\pi R_e \{ f(O) \frac{1}{k_0^2} \}$$

(3)
Disperse System of Viscoelastic Materials

If the effect of multiple scattering is neglected, it can be shown that the propagation constant \( \gamma \) and characteristic impedance \( Z \) of the disperse system containing \( N \) particles per unit volume are given respectively by

\[
\gamma = \gamma_{0} \left[ 1 - 2\pi i N \int f(\omega) \frac{1}{k_{i}^2} \right]
\]

and

\[
Z = Z_{i} \left[ 1 + 2\pi i N \int f(\omega) \frac{1}{k_{i}^2} \right]
\]

These are the fundamental formulas which are to be used below. It must be stressed that in these formulas both the effects of scattering and absorption are taken into account. Thus they are applicable not only to non-dissipative system but also to dissipative system such as viscoelastic disperse system.

Amplitude function for a viscoelastic sphere embedded in an otherwise uniform viscoelastic medium

Suppose that a spherical particle of radius \( r \) is embedded in an isotropic medium. The medium is characterized by complex bulk modulus \( K_{1} \), complex shear modulus \( G_{1} \) and density \( \rho_{1} \), and the respective quantities of the particle are \( K_{2}, G_{2} \) and \( \rho_{2} \).

We assume that the incident wave is a plane longitudinal wave propagating in the direction of positive z-axis (unit vector \( \hat{e}_{z} \)), the displacement vector of which is given by

\[
\vec{S}_{0} = e^{-ik_{i}z + i\omega t} \hat{e}_{z}
\]

Then, by solving the equations of motion of viscoelastic media under appropriate boundary conditions we obtain the "irrotational part" of the displacement vector of the scattered wave in the form

\[
\vec{S}_{s} = -V \vec{F}_{s}, \quad \vec{F}_{s} = \sum_{m \geq 0} A_{m} \bar{h}_{m}(k_{i}r) \bar{p}_{m}(\cos \theta)
\]

where \( \bar{h}_{m} \) is the spherical Bessel function of the third kind and \( \bar{p}_{m} \) is the Legendre function. \( A_{m} \)'s are determined by the boundary conditions at the surface of the particle and are expressed as functions of

\[
k_{i} = \left[ (k_{i} + \frac{q}{2} G_{i}) \frac{1}{\rho_{i}} \right]^{1/2}, \quad k_{i} = \left[ G_{i} \frac{1}{\rho_{i}} \right]^{1/2}, \quad i = 1, 2; \quad \Omega = \frac{\rho_{2}}{\rho_{1}}, \quad {\mathfrak{f}} = G_{2}/G_{1}
\]

and the radius of sphere \( r \). The boundary value problem is similar to the case of elastic system.

From the asymptotic form of the Bessel function \( \bar{h}_{m}(k_{i}r) \) for \( |k_{i}r| \gg 1 \), it is possible to determine the "amplitude function" from which we obtain

\[
C_{ext} = C_{ext,1} + 4\pi \Re \left\{ \frac{1}{k_{i}^2} \sum_{m=0}^{\infty} i^{-m} A_{m} \right\}
\]
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\[
\Gamma' = \sum_{n=0}^{\infty} \zeta_n \left( 1 - 2\pi N \frac{1}{k_r^2} \sum_{m=0}^{\infty} i^m A_m \right)
\]

\[
Z = Z_1 \left( 1 + 2\pi N \frac{1}{k_r^2} \sum_{m=0}^{\infty} \frac{(-i)^m A_m}{k_r^2} \right)
\]

The velocity \( \nu \) and amplitude attenuation coefficient \( \alpha \) of the wave in the disperse system can readily be obtained from \( \Gamma' \) as

\[
\nu = \omega \left( \frac{\beta}{\alpha} \right)^{1/2}, \quad \alpha = \Re \Gamma'
\]

Some particular cases

We have computed \( A_i \)'s for the case where

\[
|k_1 a| \ll 1, \quad |k_2 a| \ll 1, \quad |k_2 a| \ll 1
\]

and the magnitude of \( |k_1 a| \) is arbitrary. The first three terms are

\[
A_0 = \frac{i}{3} \left[ 1 - \frac{3\left( \frac{k_1}{k_2} \right)^2}{\beta (k_2)^2 - 4(\beta - 1)} \right] \frac{1}{k_1} (k_1 a)^3
\]

\[
A_1 = \frac{a_0 - 1}{(2\alpha + 1) - 6(\alpha - 1)} \left[ \frac{1 + i\beta}{3 + 3i\beta - \beta^2} \right] \frac{1}{k_1} (k_1 a)^2
\]

\[
A_2 = \frac{5}{3} \frac{\beta - 1}{\beta - 1 + \frac{1}{2} \frac{1}{k_1} (k_1 a)^3}
\]

\[
y = k_1 a, \quad f(y) = \frac{\frac{3}{2} + 3i\beta - \beta^2}{1 + i\beta}, \quad g(y) = \frac{\frac{3}{2} + 1 + iy}{\frac{3}{2} + 1 + iy - \beta^2 - iy^2}
\]

The remaining terms are higher order terms in \( |k_1 a| \), \( |k_2 a| \) and \( |k_1 a| \).

The above formulas are valid except for the case in which \( \alpha \gg 1 \) and \( |k_1 a| \ll 1 \) hold simultaneously.

If \( \alpha \gg 1 \) and \( |k_1 a| \ll 1 \), the leading term is

\[
A_1 = -i \frac{3}{k_1} \frac{1}{1 + 2\left( \frac{k_1}{k_2} \right)^2} (k_1 a)
\]

From eqs. (10), (14), (15), (16) and (17) we obtain the formula for the propagation constant which holds for the case in which \( |k_1 a| \ll 1, |k_2 a| \ll 1 \) and \( |k_1 a| \ll 1 \) and \( \omega \gg 1 \) and \( |k_1 a| \ll 1 \) do not hold simultaneously,

\[
\Gamma' = \Gamma' \left( 1 - \frac{1}{2} \frac{K_2 - K_1}{K_2 + \frac{4}{3} G_1} \right) + \frac{1}{2} \frac{3(\alpha - 1)}{(2\alpha + 1) - 6(\alpha - 1) + \frac{1 + iy}{3 + 3i\beta - \beta^2}}
\]

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\[
\phi \equiv N \frac{\phi_T}{3} \alpha^3
\]

Let us consider some extreme cases. In the above equation, if we assume that \( \kappa_1, G_1, K_2, G_2 \) are positive real constants, then we have the formula for elastic disperse systems; if we put \( G = i\omega \eta \) (\( \eta \) is a positive real constant), we have the case in which the medium surrounding the particle is viscous fluid; if we put \( \kappa_2 \to \infty, G_2 \to 0, p_2 \neq \infty \), then we obtain the case of "free" rigid particles; if we put \( \kappa_2 \to \infty, G_2 \to 0, p_2/k_2 \to 0, p_2/G_2 \to 0, \) we have the case of fixed rigid particles; and if we put \( \kappa_2 \to \infty, G_2 \to 0, p_2/k_2 \to 0, p_2/G_2 \to 0 \) we have the case of spherical cavity.

Thus the above equation contains the formula given by Ying and Truell for the case in which elastic spheres (including rigid particles and holes) are dispersed in an elastic medium as well as the formulas of several authors for the case of particles suspended in fluids, viscous or non-viscous, as particular cases.

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Pressure Dependence of Sound Velocity
in Polyethylene

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Introduction
Pressure dependence of sound velocity or elastic modulus in solids and liquids gives useful information on the anharmonicity of intermolecular potential. The aims of this paper are to measure pressure dependence of sound velocity in polymer solids and to describe thermal expansion and thermal conductivity of polymers in terms of the anharmonicity parameter. ¹

Experimental
A block diagram of the high pressure apparatus is sketched in Fig.1. Pressure in the high pressure chamber of the intensifier was measured with a manganin resistance gauge. Benzine was used as the transmission oil to the pressure cell.

The acoustic line in the pressure cell consists of the sample of polyethylene (crystallinity = 55%) with dimensions of 0.85 cm thickness and 1.0 cm diameter, sandwiched between two aluminum buffer rods, each being 2.0 cm in length. A pair of X-cut quartz transducers were cemented on each end of the acoustic line, respectively.

Pulsed longitudinal waves at 3 MHz were transmitted through the line and the received, unrectified signal was displayed on the oscilloscope. The time shift of the signal, Δt, with increasing pressure was measured on the photograph of oscilloscope pattern and the velocity change in the sample was calculated. Sound velocity of the sample at atmospheric pressure was measured as a function of temperature by the usual pulse method employing methyl alcohol as a buffer liquid.
Pressure Dependence of Sound Velocity in Polyethylene

Fig. 1. Block diagram of high pressure apparatus.

Results

Results are represented in Fig. 2, where breaks appearing in the curves above -22°C indicate the glass transition of amorphous phase.

Pressure dependence of glass temperature \( T_g \) has the slope of \( 2.2 \times 10^{-2} \) deg/atm (Fig. 3). According to the free volume theory, this slope is expected to be equal to \( \beta_f/\alpha_f \), where \( \beta_f \) and \( \alpha_f \) are contributions of free volume to compressibility and thermal expansion coefficient, respectively. In case of polyethylene, \( \alpha_f = 3.2 \times 10^{-4} \) deg\(^{-1}\) and \( \beta_f = 0.9 \times 10^{-5} \) atm\(^{-1}\) from other sources and the ratio is nearly equal to the observed \( (\partial T_g/\partial P) \) value.

The Gruneisen constant \( \gamma \) which reflects the anharmonicity of intermolecular potential is related with sound velocity \( u \) in the Debye approximation as

\[
\gamma = \frac{1}{u} \frac{\partial u}{\partial p} = \frac{1}{\beta} \left( \frac{3}{\beta} \right) \quad (\beta = \text{isothermal compressibility}). \quad (1)
\]

Values of \( \gamma \) calculated from the data in Fig. 2 are shown in Fig. 4. In doing this, the slope above the glass transition pressure...
where the amorphous phase is not rubbery but glassy was employed so that the effect of amorphous phase might be lessened. Values of γ for two glassy polymers, poly(methyl methacrylate) and polystyrene are also plotted in Fig. 4, calculated from the data by Hughes et al.\textsuperscript{4} in which longitudinal and transverse waves have the same pressure coefficient and hence give the same γ value. The value of γ in three polymers is fairly large compared with ionic crystals and metals and increases with increasing temperature.

**Thermal expansion**

Polymer crystals are characterized by strong anisotropy of binding forces among units, i.e., intrachain force constant $f$ is much larger than interchain one $g$. This anisotropic lattice is reduced to an isotropic one, in the latter of which each lattice point represents $N$ units (segment) along chain axis of the former ($N^* = 2(f/g)^{1/2}$). Vibrations of the reduced lattice correspond to the interchain modes of the original lattice, i.e., modes whose frequencies are governed predominantly by the interchain potential. Anharmonicity of crystalline force field is assumed to be related with interchain potential alone. This assumption is reasonable because thermal expansion of polymer crystals is much smaller along chain axis than in the plane perpendicular to it.

According to above considerations, the Grüneisen equation\textsuperscript{2} for polymer crystals\textsuperscript{3} is
\[ \alpha = \gamma \beta C_{\text{inter}}, \]  
(2)

where \( \alpha \) is the thermal expansion coefficient and \( C_{\text{inter}} \) the contribution of interchain vibrations to specific heat. At room temperature where the condition \( T \gg \Theta \) holds (\( \Theta \) = Debye temp. of interchain vibrations), \( C_{\text{inter}} \approx 3 \beta k/m^* \) (Dulong-Petit's law, \( k \) = Boltzmann constant, \( \beta \) = density, \( m^* \) = molecular weight of a segment). Using values of \( \alpha, \beta, \gamma \) and \( \Theta \), we can estimate \( m^* \) and \( N^* \) from eq. (2) as shown in Table 1. The value of \( m^* \) is consistent with that from force constants.

**Thermal conductivity**

In crystalline polymers at high temperatures where the mean free path of phonons is governed by the umklapp process due to anharmonicity of crystalline force field, Leibfried-Schloemann's equation \(^5\) for the reduced isotropic lattice is

\[ K = \frac{2.4 \times 10^5}{10^3 \Theta} \left( \frac{k}{\hbar} \right)^3 \frac{m^* \alpha \Theta^3}{T}, \]  
(3)

where \( K \) is the thermal conductivity, \( \alpha \) the lattice spacing and \( \hbar \) the Planck constant. The value of \( K \) for highly crystalline polyethylene above \( 120^\circ \text{K} \) is inversely proportional to \( T \) as predicted by eq. (3). \(^6\)

Using the value of \( \gamma \) in Fig. 4, \( a = 7 \) \AA, and \( m^* \Theta^3 \) value obtained from low-temperature specific heat, we obtain \( K = 1.0 \times 10^{-3} \text{cal/s/cm/deg} \) at \( 234^\circ \text{K} \), which agrees in the order of magnitude with the observed value \(^6\) extrapolated to 100% crystallinity, \( K = 2.1 \times 10^{-3} \text{cal/s/cm/deg} \). The discrepancy between calculated and observed values may come partly from temperature variation of \( m^* \). The \( m^* \) value in calculation is obtained from specific heat below \( 4^\circ \text{K} \) but \( m^* \) should increase with increasing temperature on account of decrease in \( g \). Another reason for the discrepancy may be that the theory does not take into account the high conductivity along chain axis due to intrachain lattice waves.

**References**


On Dynamic Elasticity of Reinforced Plastics.

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In recent years, reinforced plastics have been used in various fields as a new material. But there are few systematic investigations on their dynamic properties and acoustical behavior.

In the present paper, the measuring results on the dynamic elasticity of the polyester resin and their dependencies on temperature and frequency are related. The resin is reinforced by various amounts of glass fibers.

To speak briefly, a thin sample bar (about $30 \ cm \times 1.0 \ cm \times 0.5 \ cm$) is clamped by means of the upper clamping arrangement for "clamped-free" operation. At the free end the bar is exited and its vibration is detected by a pick-up transducer or a condencer microphone. The output from the transducer is recorded by a high speed level recorder. Measurements are made at the different resonant frequencies of the sample bar. The elasticity $E$ which is the real part of the dynamic elasticity $E' = E(1 + jd)$ is computed in the first approximation by Eq.(1).

$$E = 48 \pi^2 \rho \left( \frac{L^2}{h \cdot k_n} \right)^2$$  (1)

where $E$=elasticity in dyns.cm$^2$, $\rho$=density of the sample bar in grams.cm$^3$, $L$=free length in cm, $h$=thickness of the sample bar in cm,
On Dynamic Elasticity of Reinforced Plastics.

$f_n$=resonant frequency in sec$^{-1}$, and $k_n$=coefficient depending on the mode number. On the other hand, the damping factor $d$ is determined by Eq.(2).

$$d = \frac{D}{27.29 f_n}$$  (2)

where $D$=decay rate in dB·sec$^{-1}$, and is determined from the decay curve recorded by a high speed level recorder.

The material after hardening approaches gradually to the stable state as time is passing. Fig.1. shows the variation of $E$ and $d$ with time. $N$ is the value showing the amounts of glass fiber added to the resin, and $N=0$ denotes that no glass fiber is added to.

![Fig.1 Variation of E and d with time.](image)

The measurements, described in this paper, are made in the stable state of the sample bar. The temperature and frequency are ranged from about 10$^0$ to 40$^0$ centigrade and 20 c/s to 10$^4$ c/s, respectively.

Fig.2(a) shows the elasticity $E$ against frequency($f$) for a temperature of 31$^0$C. Damping factor is shown by Fig.2(b) as a function of 1/$f$. From these figures, it follows that when temperature and $N$ are constant, $E$ has no dependence on frequency, but $d$ is proportional to 1/$f$. And as for $E$, we take the simple arithmetical mean and $d = A + B/f$ as for $d$.  

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By the use of these relationships, $E$ and $d$ at a given frequency are determined as a function of temperature and $N$. For example, Fig. 3 shows $E$ (independent of $f$) and $d$ at 1,000 c/s against the inverse of the absolute temperature $T$. In this figure, the temperature depend-

![Graphs showing elastic constant $E$ and damping factor $d$ as functions of frequency and temperature.](image)

Fig. 2. Elastic constant $E = E(1 + jd)$ against frequency. $N$ represents the amount of glass fiber. (a) Real part or Young's modulus, (b) damping factor.
ence of $E$ is not so significant. On the other hand, for $d$, the relationship

$$\log d = A' + B'/T$$

is admitted in this temperature range, and this relationship is the same one as that between the coefficient of viscosity of fluid and temperature.

From these results, it is assumed that the variation of $d$ is complicated with the amount of glass fiber added to the resin. For $E$, however, Fig. 4 shows a linear variation with the volume per-cent of fiber ($V_g/V \times 100\%$, where $V=total\ volume\ of\ resin\ and\ glass\ fiber$, $V_g=volume\ of\ glass\ fiber$), and this relationship has been obtained in the static properties, for example in the tensile strength, of this kind of materials.

The scientific meaning of the coefficient of the relationships ($d = A + B/f$ and $\log d = A' + B'/T$) is under consideration.

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Fig. 3. Elastic constant against absolute temperature.

Fig. 4. Variation of $E$ with amount of glass fiber.
A NON-CONTACT MEASUREMENT OF RADIATOR VIBRATION MODE

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Introduction

A mechanical vibration pickup is often used for measuring the vibration mode of a dynamic speaker cone, but it has a problem that the mode is influenced by its mechanical impedance. Some non-contact measuring devices, such as electrostatic pickups, show excellent characteristics, but they have still problems in keeping good signal to noise ratio. The author has theoretically discussed a non-contact method of measuring sound pressures at some points in the field.

In this paper a theoretical description is given for a method to approximate the vibration mode of circular radiator set on an infinite plane baffle. The method estimates the mode by the sound pressure at some points in the sound field. The discussion in this paper is limited to the case that the sinusoidal vibration is completely in or out of phase, and its amplitude varies monotonously from the center to the edge.

Symbols

- $p^r$ sound pressure normalized by $p_0$
- $\rho$ density of the medium
- $k$ wave constant
- $i$ imaginary unit
- $U(r)$ exact velocity distribution function
- $V(r)$ approximate velocity distribution function
- $u(r)$ unit step function
- $a$ radius of circular radiator

Principle

The sound pressure produced by the circular radiator vibrating on an infinite rigid plane baffle (Fig. 1) is expressed as follows:

$$p^r(x, z) = i \int_0^{2\pi} \int_0^a U(r)e^{-ikR} \frac{R}{r} r dr d\phi$$

(1)
where \( R = R(r, x, z) = (r^2 + x^2 + z^2 - 2xr \cos \phi)^{1/2} \) (2)

Approximating the exact velocity distribution function \( U(r) \) by a stair case function \( V(r) \)

\[
V(r) = \sum_{k=1}^{M} \Delta V_k \cdot u(r_k - r)
\]
(3)

the complex sound pressure \( p^*(x, z_j) \) at a point \((x, z_j)\) in the field produced by \( V(r) \) is computed by the following expression (4)

\[
p^*(x, z_j) = \sum_{k=1}^{M} A_{jk} \cdot \Delta V_k = \sum_{k=1}^{M} (A_{jk}, r + iA_{jk}, i) \Delta V_k
\]
(4)

where

\[
A_{jk, r} = \int_0^a \int_0^b \frac{1}{r_{jk}} \left\{ \frac{\sin(kR_{jk})}{\cos(kR_{jk})} \right\} r dr d\phi
\]
\[
A_{jk, i} = \int_0^a \int_0^b \frac{1}{r_{jk}} \left\{ \frac{\sin(kR_{jk})}{\cos(kR_{jk})} \right\} z dr d\phi
\]
\[
R_{jk} = R(r_k, x, z_j)
\]
(5)

In short, \( p^*(x, z_j) = p_j \) are given by the linear combinations of \( A_{jk} \)

\[
(A_{jk}) (\Delta V_k) = (p_j)
\]
(6)

therefore an approximate function \( V(r) \) will be given by minimizing the error \( E \) defined, for example, as

\[
E = \sum_{j=1}^{N_s} (p_j^* - p_{oj})^2
\]

with the exact values \( p_{oj} = p_{o}^*(x_j, z_j) \) and letting \( M = N \), we get simultaneous linear equations

\[
(A_{jk}) (\Delta V_k) = (p_{oj})
\]
(7)

where \( A_{jk} \) and \( p_{oj} \) are real or imaginary parts of \( A_{jk}^* \) and \( p_{oj}^* \) respectively. The solutions of eq. (7) i.e. \( \Delta V_k \) \( (k=1, 2, \ldots, M) \) and expression (3) give an approximate velocity \( V(r) \). In the following sections \( U(r) \) is assumed as follows,

\[
U(r) = U_g = 1 - \frac{r^2}{a^2}
\]
(8)

(a) Axial array \((x_j=0)\)

In this case, all the sample points are put on the z-axis, then \( A_{jk} \) represents axial sound pressures produced by the circular piston motion with radius \( r_k \) and unit velocity, namely

\[
A_{jk, r} = \cos k\pi - \cos k\pi
\]
\[
A_{jk, i} = \sin k\pi - \sin k\pi
\]
\[
d_{jk} = (x_j^2 + r_k^2)^{1/2}
\]
(9)
A Non-contact Measurement of Radiator Vibration Mode

The ratios $A_{jk}/A_{hk}$ (k=1,2,...,M) become almost independent of $n_k$ when $ka$ is smaller than approximately 2 (Fig.2), then the solutions $\Delta V_k$ do not give any passable approximation. This is because the axial pressure distribution by $U_p$ does not differ much from that by $U_p$ (piston motion) for small values of $ka$. In case of $ka=10$, for example, a pretty good approximation is obtained. For better approximation, it will be a powerful technique to adopt the imaginary parts of $A_{jk}^\phi$, because they vary with $z_j$ more than the real parts.

(b) Parallel Array to X-Axis $(z_j=\text{const})$

When sample points are put on the plane of $z_j=\text{const}$., $A_{jk}$ are given by expressions (5). According to the computation results for $ka=1-20$ using imaginary parts only, this method has given better approximation than the foregoing one in Sec.(a). The error increases as $z_j$ does. For instance, when $z_j=0.5\ a$, the resultant velocity distribution $V(r)$ shows peaks and dips as depicted in Fig.3(d).

Discussions and conclusions

In general the relative error $e = V(r)/U(r) - 1$ is greater in the part with smaller velocity amplitude than in the other (Fig.4). When $U(r) = 1 - r^2/a^2$, for example, the absolute value of $\Delta V_k$ increases as $r$ does. The error of $\Delta V_k$ is, consequently, greater near the edge than near the center. When $P_i$ are three-figure-values, the obtained approximate velocity distribution $V(r)$ produces higher peaks and deeper valleys as the number of sections $M$ increases (Fig.4).
In conclusion, it is possible to estimate the vibration mode of the circular radiator by the described method, on the assumption that it vibrates symmetrically around the z-axis. For monotonous modes, for example with parabolic velocity distribution, ten sample points in the near-field are sufficient to give a good approximation. When the significant figures of sound pressures are reduced to three or four, sample points should be put very near the radiator, at the distance of 10% of the radius or less.

Acknowledgement

The author is indebted to Mr. M. Kuriyagawa and Mr. A. Kameoka for their valuable criticism and advice.

Reference

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Acousto-electric oscillations in CdSe

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It is well known that a negative dynamical resistance can arise in a semiconductor, for a suitable value of the electric field. Such a phenomenon is closely related to the amplification of sound waves that take place when the drift velocity of carriers becomes larger than the sound velocity in the sample. As a consequence a narrow region builds up, in which there exists a strong electric field and consequently a high sound intensity. Such a region travels through the sample at the sound velocity, being periodically reflected at the boundary. At the same time the current intensity flowing in the sample exhibits an oscillating behaviour. The period of such oscillations is given by

\[ T = \frac{2l}{c} \]  \hspace{1cm} (1)

\( l \) being the sample length and \( c \) the sound velocity.

Such an effect was first found in CdS and later in CdSe, previously submitted to glow-discharge.

We have performed some preliminary experiments on a CdSe monocrystal, at room temperature and for different values of the electrical conductivity. The experimental set-up is sketched in Fig. 1. The resistivity of the sample is light-controlled. A DC pulse of variable amplitude is sent in the sample. Voltage and current are then recorded through a dual-trace Sampling Oscilloscope.
Acousto electric oscillations in CdSe

With such an arrangement one can obtain directly the current/voltage characteristic at an instant arbitrarily chosen from the beginning of the pulse. In fig.2 we report two typical current pulses. The lower curve refers to a DC pulse amplitude of 400V, while the upper curve refers to a DC pulse amplitude of 750 V. In the two case the sample resistivity is the same.

Another arrangement consists in recording the current pulse shape at a fixed value of the voltage pulse amplitude. The characteristic shape of the current pulse exhibits an oscillating behaviour if the DC voltage becomes larger than a critical value at which the drift velocity of the carriers exceeds the sound velocity.

In fig.3 we collect the current-voltage characteristics. The first curve refers to the first maximum of the current pulse, (point A in fig.2) that take place for high voltage, and corresponds to a delay of about 3.5 μs.

The second curve is taken with a delay of about 5.2 μs, i.e. at the first minimum (point B).

The third curve refers to the stationary state, in which the oscillations are damped and corresponds to a delay of about 40 μs (point C).

It is evident that an Ohmic behaviour exists when V <600 Volt, while for V >600 Volt, a saturation occurs at points B and C. In
other words for V>600 Volt, the current oscillates between the ohmic value and a lower saturated value. Such oscillations are damped and the stationary state corresponds to the non ohmic behaviour.

In Fig. 4 we report the current pulse behaviour for various value of the resistivity of the sample, i.e. for various light intensities.

It results that as expected from the domains theory, the period of oscillations does not depend on the carrier concentrations. A numerical evaluation of the period gives the value of 5.1 μs. On the other hand a direct sound velocity measurement gives a value of 3.1x10^5 cm/sec. The time required for a double transit results (see eq. 1) of 5.2 μs in good agreement with the experimental period of oscillations.

The same measurements are been repeated at low temperature (76°K) without appreciable difference in results. At the same temperature a magnetic field up to 5 Kgauss does not effect the results.

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Introduction

An ultrasonic amplifier device with integrated transducers which has been proposed previously by the present authors\(^{(1)}\) exhibits an essential property of broadband characteristics because of no bonding between the transducers and the amplifying section, and also because of the prominent nature of piezoelectric semiconductor transducers. Recently, the oblique cuts of CdS crystal have been also proposed for use in ultrasonic amplifiers, as the 30° cut shows the highest electromechanical coupling for shear wave\(^{(2)}\). Combining these two useful proposals stated above, the authors have accomplished an ultrasonic amplifier device made of an obliquely cut CdS crystal with integrated diffusion-layer transducers. Electrical net gain is obtained in the frequency range from 60 MHz to 160 MHz. The maximum gain is 15 dB at 100 MHz. The fabrication technique and the experimental results of this device are described in this report.

Fabrication

A photoconductive CdS single crystal with a dark conductivity of \(10^{-7}\,\Omega^{-1}\cdot\text{cm}^{-1}\) was cut obliquely to c-axis by 60° in a form of cube approximately \(5\times5\times5\,\text{mm}^3\) and the two opposite surfaces of the cube which are 60° oblique to c-axis were polished to be optically flat and sufficiently parallel to each other. Then, the crystal was heated in indium vapor for about 30 minutes at 800°C in order to produce...
Obliquely Cut CdS Ultrasonic Amplifier

a thin and highly conductive skin. The all conductive skin was ground off except the polished end surfaces on which the diffusion-layer transducers were to be formed in the later process. A pair of copper electrodes was evaporated on these polished surfaces at a proper position by taking into account the deviation of energy flux of the ultrasonic wave. In this crystal, the deviation of energy flux of ultrasonic shear wave is about 15° from the wave normal. A pair of transducer layers was then formed by heat diffusion of some copper from the already evaporated electrodes so that a thin part of the highly conductive skin changed to be highly resistive. In Fig.1 is shown the final structure of a sample for experiment.

Fig.1. Final structure of an ultrasonic amplifier device made of obliquely cut CdS crystal with integrated diffusion-layer transducers.

Experiment

In the experiment of the ultrasonic amplification, an input transformer was employed as shown in the figure in order to provide electrical insulation from the high voltage drift field. First, the overall insertion loss of the device including the loss of the input transformer was measured in the dark. Fig.2 shows the result for a typical sample 10-B-8(4.3 x 4.1 x 2.9 mm³). The minimum insertion loss was 30 dB at 100 MHz when the transducers were tuned at each frequency, while it was 34 dB at 80 MHz when the transducers were not tuned. As is seen from the figure, a broad band characteristic was obtained as expected from the essential property of the transducer integrated ultrasonic amplifier. Fig.3 shows several examples of the observed gain characteristics for this sample when conductivity was varied. The ordinate is the ultrasonic gain in dB and the abscissa the drift voltage in kV. The three thick curves in Fig.4 show the plots of maximum gain at various frequencies when the conductivity of the crystal was kept constant at $2 \times 10^{-5}$, $4 \times 10^{-5}$ and $6 \times 10^{-5}$.
6 x 10^{-5} (\Omega \cdot \text{cm})^{-1}$, respectively.

As the values of ultrasonic gain are indicated in dB with reference to the level in the dark as 0 dB, the electrical net gain is determined by the difference between the gain and the overall insertion loss observed in the dark. When the transducers were tuned, the electrical net gain was accomplished in the frequency range from 60 MHz to 160 MHz with the value of 15 dB at the maximum, and when the transducers were not tuned, the net gain was attained in the frequency range from 60 MHz to 120 MHz with the maximum of 9 dB.

Fig.2. Experimental result of overall insertion loss in the dark.

Fig.3. Ultrasonic gain vs. drift voltage. (Sample 10-B-8)
Obliquely Cut CdS Ultrasonic Amplifier

![Graph showing maximum gain and insertion loss in dB vs. frequency in MHz.](image)

Fig. 4. Maximum gain and insertion loss in the dark. (Sample 10-B-8)

Conclusion

A pair of diffusion-layer transducers is successfully integrated on an obliquely cut CdS crystal for an ultrasonic amplifier. Although the obtained maximum ultrasonic gain is considerably smaller than that predicted by theory, the electrical net gain is still accomplished in the frequency range from 60 MHz to 160 MHz. A higher electrical net gain may be expected not only in VHF range but also in UHF range by further improvement in various techniques for crystal growth, impurity control, fabrication process or electric circuit. As a means to aid improvement, the excellent properties of evaporated-layer transducers may be useful for a UHF ultrasonic amplifier device made of obliquely cut CdS crystal as proposed in this paper.

The authors express their gratitude to Dr. M. Wada for his valuable discussion.

References


—H-84—
Excitation and Propagation of Microwave Elastic Waves in Ferroelectric Crystals.

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The piezoelectric method of excitation of acoustical waves used for the first time in 1957 by Baranski K.N. [1] still remains the fundamental method of observation of the coherent acoustic waves at microwave frequencies. The important contribution to the development of this method has been carried by Merkulov L.G. [2], Bömmel and Dransfeld [3], and also by Foster [4] who has proposed the application of thin piezoelectric films for the excitation of hyperson sound in non-piezoelectric crystals. However the transducer loss of this method is still large. Therefore the ways and possibilities of reduction of this loss are of interest.

In a general way the coefficient of the transducer loss is determined by means of joint solution of the elastic wave equations of piezoelectric crystal and of the Maxwell equations. For the one-dimensional structure we have:

\[
\begin{align*}
\left\{ 
- \omega^2 E + v_{em}^2 k^2 E &= - j \varphi \omega^2 \frac{\varepsilon}{\varepsilon_0} u \\
jk \frac{\varepsilon}{\varepsilon_0} E &= - \omega^2 u + v_{os}^2 q^2 u
\end{align*}
\]

(1)

where \(v_{em}^2 = \frac{c^2}{\varepsilon M}, v_{os}^2 = \frac{c^2_{ijkl}}{\beta}, k \) and \(q \) are the wave vectors for electromagnetic and hypersonic waves, \(\varepsilon \) and \(\varepsilon_0 \) the effective piezoelectric and dielectric constants.
Excitation and Propagation of Microwave Elastic Waves in Ferroelectric

These equations determine with $\epsilon \neq 0$ the existence of the bounded alasto-electric waves with the velocities not equal to the sound or to the light velocities.

Usually $V_{em}/V_s \sim 10^5$ and $\lambda_{em} \gg \lambda_s$ which allows to reject the first equation from (1). Then the problem is reduced to the solution of the elastic wave equation with the excitation function in the right part.

The transducer loss coefficient $A$ may be determined through the electrical impedance of the transducer. Therefore the problem is reduced to the determination of the reflection coefficient in the r.f. system. Thus

$$\Delta = 1 - \Gamma^2$$

where

$$\Gamma = \frac{Z_{tr} - Z_o}{Z_{tr} + Z_o},$$

(3)

where $Z_{tr}$ is the transducer impedance, $Z_o$ the impedance of the r.f. system. The expressions for the electrical impedances of piezoelectric transducers for the several boundary conditions are shown in Table I. The radiation resistance $r$ is usually larger than the wave resistance of an ordinary r.f. coaxial system $Z_{tr} \sim r \gg Z_o$ and

$$A = \frac{Z_o}{Z_{tr}}.$$  

(4)

One quarter waveguide or coaxial line may be considered as the impedance transformers. This property has been used in practice by Baransky and others. The optimal wave impedance of the cavity can be calculated if one knows the transducer's impedance $Z_{tr}$:

$$Z_{cav} = \sqrt{Z_{cab} \cdot Z_{tr}},$$

(5)

where $Z_{cab}$ is wave impedance of the cavity. From the known wave impedance of cavity $Z_{cav}$ we may determine the transducer's loss. Since $Z_o = \frac{Z_{cav}^2}{Z_{cab}}$ therefore

$$A = \frac{2Z_{cav}^2}{Z_{tr} \cdot Z_{cab}}.$$  

Now the transducer's loss may be decreased by the increasing of the cavity wave impedance.

Using the data of Table I for the case of excitation from the
Excitation and Propagation of Microwave Elastic Waves in Ferroelect.

surface (line one), we find the following relation

$$ A = \left[ 1 + \frac{1}{2} \left( \frac{Q_0 L_0}{C_0 + C_{t_0} - t} \right)^{-1} \right]^{1/2} = \frac{Q_0}{L_0} \sqrt{\frac{L_0}{C_{t_0} + C_0}}, $$

(7)

where $Q_0$ is given for an unloaded cavity; $L_0$ and $C_0$ are the efficient inductance and capacitance of the unloaded cavity;

$$ A = \frac{K^2}{F} Q_0 F, $$

(8)

where $F = C_{t_0} (C_{t_0} + C_0)^{-1}$ is the filling coefficient of the resonance cavity. The calculation should be similar to the other transducer circuits in Table I.

The experiments performing have been made for the hypersound excitation at the frequencies $0.5 \times 2.8$ KMC/sec in the single crystals of lithium niobate and tantalate. Also the CdS-films have been used for the excitation in $\Omega_2 0_3$, $\Omega_3 0_5 0_{4a}$, $\Omega_1 0_2$ and other non-piezoelectric crystals. The quarter-wave coaxial resonance cavities with $Q_0 = 150 \pm 200$ and the slow wave spiral system provided the minimum transducer loss about 20-35 dB (See in Ref. [5] detailed description). The strong difference in the propagation character of hypersound in single domain crystals of lithium metaniobate and polydomain crystals could be noted especially (See Fig. 1 and 2, also Ref. [5]). The presence of many ultrasound sources placed on the domain walls in electric field should be supposed. The observed behaviour a polars to be the result of interference from these randomly placed sources. The situation changed when the excitation in polydomain sample was fulfilled from outside source i.e. from a quartz plate. Then the pulse series become correct (See Fig. 3).

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Excitation and Propagation of Microwave Elastic Waves...

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Table 1.

<table>
<thead>
<tr>
<th>Transducer circuit</th>
<th>Impedance</th>
<th>C</th>
<th>R</th>
<th>( \gamma )</th>
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<td><img src="image2.png" alt="Image 2" /></td>
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Fig. 1.  Fig. 2.  Fig. 3.
Elastic and Piezoelectric Properties of Paratellurite

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Philips Zentrallaboratorium GmbH, Aachen, German Federal Republic

Introduction

We have successfully grown large single crystals of Paratellurite \( \text{TeO}_2 \). This material has some unusual piezoelectric, elastic and optical properties, which will be described here.

Crystal growing

Two modifications of \( \text{TeO}_2 \) exist and can be found in nature. Only one of them, the tetragonal form, belonging to the point group \( D_4 \) could be synthesized in laboratory. Its crystal structure has been determined by Leciejewicz\(^1\) in 1961. The crystal has no center of symmetry, thus being piezoelectric. It is optically active. The melting point of \( 735^\circ \text{C} \) is relatively low as compared with other piezoelectric or ferroelectric crystals like \( \text{LiNbO}_3 \), \( \text{LiTaO}_3 \) or \( \text{Bi}_4\text{GeO}_{12} \).

The crystals were grown as well hydrothermally as by the Czochralski method. The last method yielded large crystals of 60 mm in length and 25 mm in diameter. Fig. 1 shows the crystal pulling apparatus schematically. A crucible (a) of platinum heated electrically by (b) contains the melt of \( \text{TeO}_2 \) from which the crystal (c) is

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\( -H-89- \)
pulled by the rotating spindle (d).

Some crystals were grown along the c-axis and others along one of the a-axes.

Optical properties

The crystals are transparent and birefringent. The transparency appears from 0.35 μm wavelength in the ultraviolet up to 5 μm in the infrared. The refractive indices, using the light of the yellow sodium line are $n_e = 2.430$ and $n_o = 2.274$, much higher than in most other transparent materials. Also the optical activity is very high, it has been measured to be $103^\circ \text{mm}^{-1}$. The material is being investigated for nonlinear optical effects.

Elasto-electric properties

The essential peculiarity of TeO$_2$ is its high degree of symmetry, the elasto-electric matrices being shown in Fig. 2.

$$
\begin{pmatrix}
\varepsilon_1 & 0 \\
0 & \varepsilon_1 \\
0 & 0 & \varepsilon_3
\end{pmatrix}
\begin{pmatrix}
0 & 0 & 0 & \varepsilon_{14} & 0 & 0 \\
0 & 0 & 0 & 0 & \varepsilon_{14} & 0 \\
0 & 0 & 0 & 0 & 0 & 0
\end{pmatrix}
\begin{pmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{12} & \varepsilon_{11} & \varepsilon_{13} & 0 \\
\varepsilon_{13} & \varepsilon_{13} & \varepsilon_{33} & 0 \\
0 & 0 & 0 & \varepsilon_{44}
\end{pmatrix}
\begin{pmatrix}
\varepsilon_{66}
\end{pmatrix}
$$

Fig.2 Elasto-electric matrices of point group D$_4$

Using the pulse-echo method and resonance methods with different crystal cuts, including oblique ones, we have determined the elastic constants and their temperature dependence. The measured dielectric, piezoelectric and elastic constants at room temperature and their tolerances are given in Table 1. The dielectric constants are unusually high for non ferroelectric crystals. The value of the piezoelectric constant should be regarded as preliminary.
Elastic and Piezoelectric Properties of Paratellurite

Table 1

<table>
<thead>
<tr>
<th>$e_{11}$</th>
<th>$e_{33}$</th>
<th>$e_{14}$</th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{13}$</th>
<th>$c_{33}$</th>
<th>$c_{44}$</th>
<th>$c_{66}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5</td>
<td>25</td>
<td>0.23</td>
<td>5.6</td>
<td>5.16</td>
<td>2.72</td>
<td>10.51</td>
<td>2.70</td>
<td>6.68</td>
</tr>
<tr>
<td>+4%</td>
<td>±5%</td>
<td>±20%</td>
<td>±3%</td>
<td>±3%</td>
<td>±6%</td>
<td>±3%</td>
<td>±2%</td>
<td>±2%</td>
</tr>
</tbody>
</table>

Acoustic properties

Two remarkable facts can be derived from Table 1:

1) $c_{66} > c_{11}$; the fast shear wave propagating in <100> direction has a higher sound velocity than the compressional wave in the same direction.

2) Calculations show the existence of a pure shear wave in <110> direction polarized perpendicularly to the c-axis, its phase velocity being determined by the effective elastic constant $c' = \frac{1}{2} (c_{11} - c_{12})$. It follows from Table 1 that the phase velocity of this wave is exceptionally small, $v' = 0.6 \times 10^5$ cm sec$^{-1}$. This has been proved experimentally and may be useful in delayline applications.

Due to the high symmetry of TeO$_2$ one expects piezoelectric excitation of only one shear mode being almost free of coupling to other modes if oblique cuts are avoided. Longitudinal modes cannot be excited except in oblique cuts. The piezoelectric tensor is invariant with respect to rotation about the c-axis. Thus purely torsional waves can be excited by setting up a radial electric field in a cylindrical specimen the axis of which coincides with the c-direction of the crystal. Fig. 3 shows two possible configurations for the excitation of torsional waves. We have made torsional resonators from 70 kHz up to the MHz range. All resonance curves are almost free of spurious resonances. The piezoelectric coupling factor for the pure shear wave excitation is in the order of 10%.

Fig. 3
Torsional resonators (Cylindrical symmetry about c-axis)
Elastic and Piezoelectric Properties of Paratellurite

The temperature coefficients of the resonance frequencies indicate that there are cuts with zero temperature coefficient. We are going to compute these special directions. We expect, however, that the piezoelectric coupling factor in these directions may be low.

Preliminary measurements of the ultrasonic attenuation at 30 MHz resulted in $Q = 10^4$ for the very slow shear wave in $<110>$ direction and $Q = 3.4 \cdot 10^3$ for the piezoelectric active shear wave in $<001>$ direction.

Temperature Dependence of Ultrasonic Amplification in CdS and its Relationship to Electron Trapping Effects.

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Introduction
Temperature dependence of ultrasonic amplification in CdS crystals is fully investigated over a temperature range from 80°K to 300°K. The attenuation-amplification characteristics in relation to the drift field at low temperatures deviate considerably from the small signal theory in which no trapping has been taken into account. The characteristic curves become asymmetric with reference to the crossover drift field.

In a previous paper (1) we have already presented the effect of electron trapping on the electron drift mobility as a function of temperature. The details of gain characteristics, however, were not shown in the paper. In this report, theoretical considerations are extended to the attenuation-amplification characteristics and it is found that when two different kinds of electron trapping levels are theoretically introduced, the observed characteristics are well explained.

Specimen
The specimens used were cut from highly conductive CdS crystals and heated carefully in sulfur vapor. The original crystals were grown from the melt and had electron density \( n = 3.6 \times 10^{17} \text{ cm}^{-3} \) and Hall mobility \( \mu_H = 300 \text{ cm}^2/\text{volt}\cdot\text{sec} \) at room temperature. From the temperature variation of \( n \), it was observed that the crystals had a shallow donor level with an activation energy of 0.03 eV.

Fig.1 gives the curve of thermally stimulated current for a typical CdS crystal used in the ultrasonic amplification experiments. The peak at 105°K is the most prominent and the corresponding trap depth \(^{(2)}\) is about 0.17 eV.

Experiment
The amplification experiments are made with ultrasonic shear waves of 60 MHz.
Fig. 2 shows typical gain vs. drift field curves observed at various temperatures. Although a crystal conductivity is kept constant, the gain characteristics vary remarkably with temperature. As the temperature is lowered from room temperature to 200°K or 171°K, both the maximum gain \( G_{\text{max}} \) and the maximum loss \( G_{\text{min}} \) decrease and the curves become considerably asymmetric with regard to the cross-over drift field. However, at further lower temperature 93°K, a tendency to restore the symmetric nature is observed. The ratio \( r \equiv \frac{G_{\text{max}}}{G_{\text{min}}} \), which is employed as a measure of the symmetry, is plotted in Fig. 3 as a function of temperature. A minimum and a maximum appear in \( r \) at 140°K and 105°K, respectively.

**Theoretical Analysis**

In order to explain the observed results, let us try to introduce the temperature dependence of electron trapping effect into the amplification theory. From a previous theory\(^{(3)}\), \( r \) is given as follows:

\[
r = \left( \frac{\sqrt{1+Q^2} - Q}{a} \right)^2,
\]

where \( a \) is the ratio of imaginary part to real part of the complex trapping factor \( f \). In the case of multiple trapping levels having different energy \( E_m \), density \( N_m \) and attempt-to-escape frequency \( \nu_m \), \( f \) can be derived from the trapping kinetics under the steady-state equilibrium condition between the electrons in the conduction band and each trapping level and is obtained as follows:

\[
f = \left[ 1 + \sum \frac{N_m}{N_c} \frac{(1-F_m)^2}{\exp(-E_m/kT)+\beta_m(1-F_m)} \right]^{-1},
\]

where \( \beta_m = \omega/\nu_m \) (\( \omega \) is the angular frequency of an ultrasonic wave) and \( N_c \) is the conduction band density of states which is equal to \( 4.24 \times 10^{14} \text{T}^{-3/2} \text{cm}^{-3} \) for CdS with \( m^* = 0.2m_e \).\(^{(4)}\) \( F_m \) is the Fermi distribution function for m-th trap level and can be expressed by \( F_m = [1 + \exp(E_f-E_m)/kT]^{-1} \), where \( E_F \) is the Fermi energy measured from the bottom of the conduction band.

Let us first consider only one kind of trap level \((E_f, N_f, \nu_f)\) whose energy depth is shallow enough so that \( F_f \ll 1 \), that is, Boltzmann distribution is assumed.
Temperature Dependence of Ultrasonic Amplification in CdS

For this trap level, \( a_1 \) is obtained from Eq.(2) as follows:

\[
Q_1 = \beta_1 \cdot \left[ \frac{N_c}{N_1} \left\{ \beta_1^2 + \exp(-2E_1/kT) \right\} + \exp(-E_1/kT) \right]^{-1}.
\]  \( \text{(3-a)} \)

As \( N_c = T^{3/2} \), \( a_1 \) increases with the decrease of the temperature. As is easily found in Eq.(1), \( r \) decreases monotonously with the increase of \( a_1 \), and therefore, the trap level of this kind acts simply to destroy the symmetry when the temperature is lowered.

![Fig. 2 Observed gain vs. drift voltage at various temperatures.](image)

Fig. 2: Observed gain vs. drift voltage at various temperatures.

![Fig. 3 Observed data and theoretical curves for \( r = |G_{\text{max}}/G_{\text{min}}| \) as a function of temperature. The thick curve is obtained by taking into account two trap levels. The other two thin curves 1 and 2 are for reference showing the characteristics when a single trap level is taken into account: Curve 1 for \( E_1 = 0.03 \text{ eV} \) and Curve 2 for \( E_2 = 0.15 \text{ eV} \), respectively.](image)

Fig. 3: Observed data and theoretical curves for \( r = |G_{\text{max}}/G_{\text{min}}| \) as a function of temperature. The thick curve is obtained by taking into account two trap levels. The other two thin curves 1 and 2 are for reference showing the characteristics when a single trap level is taken into account: Curve 1 for \( E_1 = 0.03 \text{ eV} \) and Curve 2 for \( E_2 = 0.15 \text{ eV} \), respectively.

Next, let us consider the trap level \( (E_2, N_2, \nu_2) \) for which the electron occupation is expressed by the Fermi distribution function. The term \( \exp(-E_2/kT) \) in Eq.(2) can be neglected at low temperatures, then we obtain

\[
Q_2 = \frac{1}{\beta_2} \cdot \frac{N_2}{N_C} (1-F_2).
\]  \( \text{(3-b)} \)

If we assume an approximate thermal equilibrium of electrons under steady-state excitation with regard to the trap level, \( a_2 \) can be expressed as follows:

\[
Q_2 = \frac{1}{\beta_2} \cdot \frac{N_2}{N_C} \left\{ 1 + 10^{-2} \sigma_0 \exp(E_2/kT) \right\}^{-1}.
\]  \( \text{(3-c)} \)

in which \( \mu = 284 \cdot (T/300)^{3/2} \text{ cm}^2/\text{volt} \cdot \text{sec} \) is used. The Eq.(3-c) has a maximum as a function of temperature, and for the conductivity range \( 10^{-6} \leq \sigma_0 \leq 10^{-4} \text{ (\mu}\text{cm})^{-1} \), the corresponding temperature \( T_m \) is approximately determined as follows:

--- H - 95 ---
\[ \frac{E_2}{kT_m} \cong 3.5 - 2.1 \log \sigma_0 \]  \hspace{1cm} (4)

Using Eq.(4), we can obtain the trap depth \( E_2 \) from the temperature \( T_m \) observed in the characteristics of \( r \) for a given conductivity.

Temperature dependence of ultrasonic amplification characteristics may be theoretically obtained if the necessary factors are found by applying the above theory to the corresponding experimental data. In Fig.3, as \( T_m = 140^\circ K \) and \( \sigma_0 = 3.5 \times 10^{-5} (\Omega \text{cm})^{-1} \), then we obtain \( E_2 = 0.15 \text{ eV} \). If the minimum value of \( r \) and \( a_r \) of Eq.(3-c) is substituted in (1), the product of \( \tau_1 \) and \( \nu_2 \) is also obtained as \( \tau_1 \nu_2 = 1.2 \times 10^{26} \text{cm}^{-3} \text{sec}^{-1} \). The thick curve in Fig.3 shows the half-empirically obtained theoretical curve for \( r \) when two shallow trap levels, \( E_1 = 0.03 \text{ eV} \) and \( E_2 = 0.15 \text{ eV} \), are taken into account. Fig.4 shows the observed \( G_{\text{max}} \) and \( G_{\text{min}} \) plots in comparison with the theoretical curves as a function of temperature for various crystal conductivities.

**Conclusion**

Observed temperature characteristics of the ultrasonic attenuation and amplification in semiconductors are theoretically explained by introducing two different kinds of electron trapping levels. The trap level at \( 0.03 \text{ eV} \) is a level due to the ionized donor states which may remain unfilled during the sulfur treatment. The trap level at \( 0.15 \text{ eV} \) may be considered to correspond to the T.S.C. peak at \( 105^\circ K \).

The authors are grateful to Dr. Masanobu Wada and Dr. Tadashi Takahashi for their helpful discussions.

**References**

The action of photons on the attenuation of transversal ultrasonic waves in CdSe crystals.

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1. Introduction

When an ultrasonic wave passes through a piezoelectric semiconductor crystal, electric phenomena are observed which occur due to the alternating electric field produced by the elastic wave and the conductivity of the crystal.

A theory of the attenuation of an ultrasonic wave in a semiconducting crystal was developed first by White [3]. According to White's theory the increase the conductivity of the crystal by illumination leads to an increase of the attenuation and the velocity of the ultrasonic wave. Hine [2] observed however, that longitudinal waves in CdS crystals are attenuated to a lower degree in samples illuminated by photons. This phenomenon is of a very complicated character and is difficult to explain. Similar effects for transverse waves and a transverse wave moving in the direction perpendicular to the C axis of the crystal were found in our experiments with CdSe samples. The variation of the attenuation observed was -15 dB in the case of a sample 7 mm thick, illuminated by intense white light.

2. The measuring equipment

The equipment used is shown in Fig. 1. Its most interesting part consists of a transmitter enabling the production, in the sample, of an elastic wave of varying polarization and a receiver of the wave leaving the sample. The transmitting transducer is a Y-cut quartz plate with marked X axis, glued to a small cylinder of fused quartz.
The action of photons on the attenuation of transversal waves

This transducer is joined to the sample by means of grease, which enables rotation of the transducer together with the cylinder and transmission of a wave of suitable polarization into the sample. After passing through the crystal this wave is picked-up by a receiving transducer of similar design. Such an arrangement enables propagation of a transverse wave at any angle in relation to the axis of the crystal. The Y-cut quartz transducer is set into vibration by an electric field normal to its surface thus producing in the sample a transverse wave polarized parallelly to the X-axis of the transducer in agreement with the formula \( X_y = d_{23} E_2 \) where \( X_y \) is the shear deformation, \( d_{23} \) - the \( E_2 \) piezoelectric constant of quartz and \( E_2 \) - the electric field.

The voltage generated in the receiving transducer is at its maximum, when the direction of wave polarization is that of the X-axis of the transducer according to the relation \( V = V_0 \cos \theta \) where \( \theta \) is the angle between the X-axis of the transducer and the direction of polarization of the incoming wave and \( V_0 \) - the maximum voltage induced in the transducer.

According to the theory of propagation of elastic waves in anisotropic solids. Three waves can propagate in CdSe crystals of wurtzite structure the directions being normal to the C-axis or parallel to the a or b axis.

One of these is a longitudinal wave and the other two are transversal waves polarized in two mutually perpendicular planes.

If the transmitting transducer is set in such a way, that the direction of its X-axis is parallel or perpendicular to the C-axis of the crystal, a wave of parallel or perpendicular polarization /in relation to C-axis/ is generated.

An intermediate position of the transducer generates both wave types simultaneously, the energy of each depending on the polarization angle in relation to the X-axis of the transducer.
2. Variation of the attenuation of ultrasonic waves in a CdSe sample under the influence of photons

The sample investigated was a Wurtzite lattice CdSe crystal grown at the Institute of Physics of the Polish Academy of Science in Warsaw. The sample was cut out from the middle part of the crystal to avoid nonhomogeneity usually occurring near the surface. The thickness of the sample along the b axis was 7 mm, and, its dark conductivity — $10^{-5}$ Ω$^{-1}$ cm$^{-1}$.

Experiments were carried out by means of the pulse technique, the carrier frequency being 30 MHz and the electric pulse length — about 1 μs.

The electric pulse was amplified in a superheterodyne receiver and displayed on a synchroscope.

The investigations were carried out for three different positions of the Y-cut transmitting transducer in relation to the axis of the CdSe crystal.

The results of measurements were recorded photographically. Fig. 2 shows the block diagram of the most interesting experiment.

![Block diagram of the position of the transducers for simultaneous generation and reception of two transversal waves in a CdSe sample.](image)

The arrows on the left hand side of the figure indicate the axis b of the sample, the direction of the axis X of the transmitting transducer, and the direction of vibration/polarization of the transducer. The arrows on the right hand side of the figure indicate the corresponding directions for the receiving side. The most interesting experiment was carried out according to the diagram of Fig. 2.

The transmitting transducer was arranged in such a way that its oscillations followed the bisector of the angle formed by the c and b axis of the sample. This position of the transducer enables generation of two transverse waves, one of which is not affected by illumination when passing through the sample.
the other one being attenuation by the action of photons.

In the experiment some reduction of the attenuation of the wave in the illuminated sample is observed for a certain position of the receiving transducer. This variation amounts to -13 dB for the 7 mm sample and the position of the receiving transducer corresponding to the angle $45^\circ$ between the X-axis of the transducer and the C-axis of the sample. Fig. 3 for other values of this angle the decrease of the attenuation is smaller.

The result of this experiment seems to be interesting, since it is not covered by White's theory.

The reduction of the attenuation is due to the action of photons alone with no action of the external electric field.

References


The time-transition process of the Rayleigh wave amplitude stimulated by conductivity change of CdS crystal.

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It is hoped to obtain the information on the properties of crystal surface-layer studying transition process of interaction Rayleigh wave with conductivity electrons of CdS crystal.

The experiments were performed on the CdS crystal produced in Institute of Single Crystals (Kharkov city) by the method /1/. Rayleigh wave pulses with 3 microsec. duration and 30 Mc/s frequency propagated on the plane normal to the crystal hexagonal axis Z. Rayleigh wave excitation and reception were performed by the comb structure method /2/. It was possible to change sharply crystal conductivity $\sigma$ by switching on and off the illumination of the crystal. Besides, it was possible to change separately the conductivity of crystal thin-surface-layer, by applying to the sample constant electric field $E_0$ normal to its surface ("field effect" method, see for example /3/). This field produced in the crystal surface-layer $\approx 0.02$ mm thickness electron concentration, which significantly exceeded the volume concentration.

The results of experiments are shown in fig. 1-3. In fig.1 Rayleigh wave amplitude $A_R$ is shown versus time $t$ in minutes on
switching on and off the field $E_o$. In fig. 2 amplitude $A_R$ is shown versus time $t$ in minutes on switching on and off the crystal illumination. The moments of switching on the field $E_o$ and light are designated $t_i$ and $t_i'$, respectively. The switching off moments are $t_2$ and $t_2'$, respectively. It is seen from these graphs that, when the field and light are absent ($t < t_i$ and $t < t_i'$), the Rayleigh wave amplitude is constant. The amplitude $A_R$ decreases upon switching on the field $E_o$ and light. However, the time establishment of decreased amplitude level occurs a long time and not smoothly, but with powerful oscillations. The reestablishment of the origin amplitude level upon switching off the field $E_o$ or light ($t > t_2$ and $t > t_2'$) occurs analogous manner.

The experiment results can be easily explained on assuming electronic traps occurrence in CdS crystal. Apparently many types of traps with different relaxation time $\tau_i$ take place. Rayleigh wave amplitude oscillations indicate that traps with $\tau_i \sim 2 - 3$ min, $\tau_2 \sim 4 - 6$ min and $\tau_3 \sim 24$ min occur. Traps with much less relaxation time couldn’t be revealed by our visual oscillations observation method. We can calculate the average electron concentration in Rayleigh wave localization layer, if we know the field intensity $E_o$ and conductivity $\sigma$. Also the same concentration can be determined from experiment on decreasing the average amplitude level $A_R$, if we know the dependance $A_R(\sigma)$ for given crystal. Comparing these two average concentration values one can calculate the effective value of the trap factor $f$, which is approximately 0.06. Knowing the dependance $A_R(\sigma)$ on switching on and off light and the electric field $E_o$, we could evaluate factor $f$ for the traps with relaxation time $\tau_{i,2,3}$ by amplitude $A_R$ oscillations.
The time-transition process of the Rayleigh wave amplitude

Fig. 1-3 Results of the experiments

This factor is equal approximately 0.78.

Thus described experiments allow to obtain some information on the crystal surface-traps. These traps are located either in the Rayleigh wave localization layer ≈ 0.06 mm thickness (the experiments on Rayleigh wave amplitude establishment upon switching on and off the light) or in thinner layer of surface electric charge localization (≈ 0.02 mm) produced by the electric field $E_0$ (the experiments upon switching on and off the field $E_0$). Also it was interesting to obtain the information on volume traps placed
in the body of the crystal. For this purpose we investigated the time establishment of longitudinal wave amplitude $A_\ell$ upon switching on and off the light. This wave propagated across the crystal towards $z$ axis. The experiments were performed at the same frequency and the same crystal illumination as in the case of Rayleigh waves. The dependence $A_\ell(t)$ is shown in fig. 3. It is evident from comparing fig. 2 and 3 that the longitudinal wave amplitude oscillations are much less than the Rayleigh wave amplitude oscillations. Calculating factor $\varphi$ for traps with relaxation time $\tau_{n_z}$ by longitudinal wave oscillations amplitude, we obtain $\varphi = 0.96$. Consequently the concentration of such traps in the crystal volume $n_v$ is equal $\approx \frac{1}{\varphi} n_s$, where $n_s$ is the concentration such traps in the crystal surface layer.

Bibliography

Continuous amplification of ultra a. hipersonic surface waves in CdSe crystal with a semiconducting thin surface layer formed by the photo-effect.

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Introduction

In this paper there was analysed the problem of continuous amplification of the ultrasonic surface waves in piezo-photo-semiconducting crystals CdSe. The effect of continuous amplification was obtained by forming a thin /cooled/ surface, semiconducting layer. The layer of that type was formed by exposing the surface of the CdSe crystal to the visible light, utilizing the photo-effect phenomenon and small transparency of crystal. The idea of continuous amplifier was proposed by the author before in papers [1], [2], [3], by placing on the piezo-quartz a thin semiconducting layer. Realization of such a system meets quite a series of difficulties of technological kind. This difficulties fall now off, as the layer forms itself in a natural way. In the paper the results were obtained in a closed analytical form, due to the use of perturbation method /with some restriction on physical parameters/ [4], [5]. The theoretical results were experimentally proved in [6] and by authors collaborators in paper to be published /for impulse systems in CdS also in [7], [8]/. A model of CdSe with isotropic approximation of the elastic characteristics of medium was introduced in this paper according to [4]. The problem of direct continuous or quasicontinuous amplification of surface waves in CdS /with surface cooling/ was solved in [5].
Continuous amplification of surface waves

Fundamental equations

All the assumptions of [4] are retained. It will be assumed that the surface of the CdSe crystal is illuminated by visible light forming a conducting surface layer. It will be assumed that the wavelength is greater than the thickness of the layer, so that the latter can be treated as perfectly thin.

The set of the equations of the not illuminated part of the CdSe crystal treated as a piezoelectric will have the form

\[
\varepsilon_{ik} = \rho \varepsilon_{ik} \quad \text{and} \quad D_{ik} = 0
\]

where

\[
\begin{align*}
\varepsilon_{ik} &= c_{ik}^{(0)} u_{ik} - e_{ik} \varphi_j \\
D_{ik} &= e_{ik} \varphi_j + e_{ik} \varepsilon_{ij}
\end{align*}
\]

The equation of the surface layer and vacuum will be the following

\[
\rho \ddot{u}_i + \int V_0 \Gamma_{ik} \left( \delta \varphi_{ik}^{(0)} - \int D_{ik} \varphi_{ik} \right) = 0 \quad \text{and} \quad \nabla^2 \varphi = 0
\]

where \( \delta \varphi^{(0)} = \frac{d}{d} \) – thickness of the layer, \( \rho \) = \( \rho \mu \). Using the two way notation of the tensors \( c_{ik}^{(0)} \) and \( e_{ik} \) and taking the symmetry relations of CdSe crystal into account we get equation system for \( x_1, x_3 \) plane independent of \( x_2 \)/

\[
\begin{align*}
\rho \ddot{u}_i &= c_{ik} \varepsilon_{ik} + c_{ik} \varepsilon_{ij} + (c_{ik} + c_{kl}) \varepsilon_{ij3} - (e_{ik} + e_{jl}) \varphi_{ij} \\
\rho \ddot{u}_3 &= c_{ik} \varepsilon_{ik} + c_{ik} \varepsilon_{ij} + c_{ik} \varepsilon_{ij3} - e_{ij} \varphi_{ij3} - e_{ik} \varphi_{ij}
\end{align*}
\]

The boundary conditions take the form

\[
\begin{align*}
\varepsilon_{jk} &= 0 \quad \text{for} \quad k = 1, 2, 3 \quad \text{and} \quad D_{3} - \varphi_{3} = - \pi \rho \varepsilon_{3} \quad \varphi = \varphi
\end{align*}
\]

Simplified equations using the isotropic approximation of the elastic properties

It was shown in [4] that for crystals of the wurtzite group – in CdSe crystals in particular – the following approximate relations are valid

\[
\begin{align*}
c_{ii} &\approx c_{ij}, c_{ii} \approx \lambda + \mu, c_{ij} \approx \mu, \varepsilon_{ij} = - \varepsilon_{ij}, \varepsilon_{ii} = - \varepsilon_{33} = \varepsilon
\end{align*}
\]

Then the system (5) may be reduced to the following one

\[
\begin{align*}
\rho \ddot{u}_i &= (\lambda + \mu)(u_{ik} + u_{ij}) + \mu \varepsilon_{ij} + 2 e_{ij}, \\
\rho \ddot{u}_3 &= (\lambda + \mu)(u_{ik} + u_{ij}) + \mu \varepsilon_{ij} + 2 e_{ij}
\end{align*}
\]
Continuous amplification of surface waves

\[
\mathcal{E} \nabla^4 \varphi + 4\pi \varepsilon (2u_{13} + u_{33} - 2u_{33}) = 0
\]

\[
\dot{\varphi} + \frac{1}{2} V_0 \varphi_{rr} - 6 \varphi''_{rr} - \frac{1}{2} D_0 \varphi_{rr} = 0; \quad \nabla^2 \varphi = 0
\]

Eliminating in (8) the variables \( \varphi_{rr}, \varphi_{rs} \), we can reduce this system to one equation for \( \varphi \)

\[
\left[ \nabla^2 \Box - a_1^2 \varphi + a_1^2 \varphi \right] \varphi = 0
\]

where

\[
\Box = \alpha^2 \frac{\partial^2}{\partial t^2}; \quad a_1 = \frac{\lambda + 2\mu}{\mu}; \quad a_1 = \frac{\mu}{\rho}; \quad \varepsilon = \frac{4\pi \varepsilon}{\rho a_1^2}; \quad \kappa = \frac{4\pi \varepsilon}{\rho a_1^2}
\]

\[
G = (a_1^2 - a_1^2) \left( 15 \varphi_{rr} - 40 \varphi_{rr} \right) + \nabla^2 \varphi_{rr} + \nabla^2 (4 \varphi_{rr} - \varphi_{rr})
\]

Characteristic equation

Assuming the solution in the form

\[
\varphi = \sum_{i=1}^{3} A_i \exp(\omega x - k_i x) \exp(-\beta_j x), \quad \tilde{\varphi} = \sum_{i=1}^{3} A_i \exp(\omega x - k_i x)
\]

we get from (9)

\[
(z_j - 4)(z_j - 4) \left[ (1 + \frac{4}{m} (z_j - 1)) \left( 1 - \frac{4}{m} (z_j - 1) \right) + \kappa \left( 1 - \frac{4}{m} (z_j - 1) \right) \right]
\]

where

\[
\beta_j = k_j; \quad \xi = \frac{\omega}{2k}; \quad \kappa = \frac{m}{k}; \quad \kappa = \frac{m}{k}; \quad m = \frac{\lambda}{\mu}; \quad \kappa = \frac{m}{k}
\]

and from (6)

\[
\sum_{j=1}^{3} \left( R_{ij} + \Theta_{ij} N \right) A_i = 0
\]

where

\[
N = \frac{\Theta}{D_n \omega \kappa} \frac{A}{\varepsilon \varepsilon}; \quad R = \frac{1}{\rho} U_{0} \frac{\hat{\varphi}}{\hat{\varphi}}; \quad U_{0} = V_0 \frac{\varphi}{\varepsilon}; \quad \Theta = \frac{4\pi \varepsilon \varepsilon}{\rho a_1^2}; \quad D_n = \frac{\hat{D}_n \omega a_1^2}{\varepsilon}
\]

\[
R_{ij} = \left( \beta_j^4 - 4 + 2m \right) \left( \frac{3 \beta_j^4 - 3 \beta_j^2}{M_i} \right) - 2m \beta_j \left( 4 \beta_j^4 + \beta_j^2 \right) \left( \frac{2 \beta_j^4}{M_i} \right)
\]

\[
R_{ij} = \left( 4 + \beta_j^4 \right) \left( \frac{3 \beta_j^4 - 3 \beta_j^2}{M_i} \right) - 2m \beta_j \left( 4 \beta_j^4 + \beta_j^2 \right) \left( \frac{2 \beta_j^4}{M_i} \right)
\]

\[
R_{ij} = \left( 1 + \beta_j^4 \right) \left( \frac{3 \beta_j^4 - 3 \beta_j^2}{M_i} \right) - 2m \beta_j \left( 4 \beta_j^4 + \beta_j^2 \right) \left( \frac{2 \beta_j^4}{M_i} \right)
\]

where

\[
M_i = \left( \beta_j^4 - 4 + m \xi \right) \left( \beta_j^4 - 4 \right); \quad M_i = \left( \beta_j^4 - 4 + m \xi \right) \left( \beta_j^4 - 4 \right)
\]

The characteristic determinant takes the form

\[
W = \left\| R_{ik} + \Theta_{ij} N \right\| = 0; \quad W = \left\| W_{0} + N \right\| = W_{0} + N (\Gamma_{s} + \Gamma_{s} + \Gamma_{s})
\]

Amplification coefficient

To obtain a closed expression of the amplification the perturbation method will be used. We assume
Continuous amplification of surface waves

\[
\begin{align*}
\psi^2 &= \psi^2_0 + i\lambda; \quad \phi = \phi_0 + \delta; \quad \beta^2 = \beta_0 + \Delta \beta; \quad N = N_0 + iN_2 \\
W_0(\psi_0) &= W_0(\psi_0) + i\Delta W(\psi_0); \quad \Delta \phi_2 = \lambda \phi_2
\end{align*}
\]

We get from /15/ using the perturbation rules

\[
\begin{align*}
W &= W_0(\psi_0) + i\left[\lambda W_0(\psi_0) + \Delta \phi \frac{\partial}{\partial \phi} W_0(\psi_0)\right] + N W_0(\psi_0) = 0
\end{align*}
\]

where

\[
W_0(\psi_0) = \sum R^{(0)}_{ki} \Gamma_{ki} ; \quad W_0 = \sum R^{(i)}_{ki} \Gamma_{ik}
\]

The amplification coefficient will take the final form

\[
\lambda = \frac{N_0 W_0(\psi_0)}{W_0(\psi_0) + \sum \beta \frac{\partial}{\partial \beta} W_0(\psi_0)} = \frac{N_0}{M} \quad \left(W_0(\psi_0) = 0\right)
\]

\[
\lambda = \frac{4}{\varepsilon M} \frac{\Theta}{R} \frac{4}{1 + \frac{D_0^2}{R^2}}; \quad \lambda_{\text{max}} = \frac{4}{\varepsilon M} \frac{\Theta}{2D_0}
\]

Assuming \( k = k_0 + ik_{\phi} \), \( \frac{k_{\phi}}{k_0} = \tau \)

we get for amplification

\[
\omega = 8.63 k_0 \tau \left[\text{dB/cm}\right]
\]

For the lack of space we are not able to write explicite the perturbation formula for \( R_{ik} \), \( \Gamma_{ik} \). Many examples have been considered.

For instance for \( \omega \approx 45 \text{MHz}; \quad \theta = 10^{-5} \text{[deg]}; \quad \varepsilon \approx 10; \quad \kappa \approx 0.049; \quad D_0 \approx 5 \div 10 \)

\[
\omega = 8.5 \left[\text{dB/cm}\right]
\]

which wincides with experimental results [6].

References


Magnetic Field Dependence of Ultrasonic Attenuation 
in Piezoelectric Semiconductors

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Introduction

The ultrasonic attenuation due to conduction electrons or holes in piezoelectric semiconductors\(^1\) has been shown to be observable and depend on the electrical conductivity and the carrier mobility. Therefore, the attenuation is expected to depend strongly on the applied transverse magnetic field when the condition \(\omega_c \tau \gg 1\) is satisfied. Here \(\omega_c\) is the cyclotron frequency and \(\tau\) is the scattering time of carriers. It should be remarked, however, the magnetic field dependence of ultrasonic attenuation is not the same as that of the electrical conductivity (magnetoresistance), because the ultrasonic attenuation is determined by one of the diagonal components of conductivity tensor, while the magnetoresistance has the nondiagonal components due to the Hall effect\(^2\).

The transverse magnetic field can increase or decrease the ultrasonic attenuation depending on the magnitude of the screening effect. In the case of nearly complete screening we have a constant current system, while in the case of incomplete screening we have a constant voltage system\(^3\). Thus, in the former case the magnetic field increases the ultrasonic attenuation through the decrease of electrical conductivity\(^4\), while in the latter case the magnetic field decreases the attenuation.

In this paper we present the experimental results of the ultrasonic attenuation in GaAs and InSb which clearly show the two types of magnetic field dependence.
The experimental results are explained by the straightforward extension ² of the Hutson-White theory ¹.

Incomplete Screening Case

In order to study the incomplete screening case, we choose the sample of O₂-doped GaAs with relatively low conductivity and high mobility at room temperature and the sample of CdS at liquid helium temperature. The propagation and the polarization directions of ultrasonic waves are [110] and [001] for GaAs, and [001] and [001] for CdS, respectively. The attenuation was measured by a pulse echo technique in the frequency range of 15 – 315 MHz. In Fig. 1 the magnetic field dependence of attenuation α is shown for the sample of GaAs with the electrical conductivity \( \sigma = 2.78 \times 10^{-4} \ \text{m}^{-1} \ \text{cm}^{-1} \) and the carrier mobility \( \mu = 7.1 \times 10^{3} \ \text{cm}^{2} \ \text{V}^{-1} \ \text{sec}^{-1} \). The frequency dependence of the magnetic field effect \( (\alpha(H) - \alpha(0)) \) is shown in Fig. 2. The attenuation decreases with increasing the magnetic field in the frequencies higher than 45 MHz, while the attenuation increases with the magnetic field at 15 MHz. In the present case the dielectric relaxation frequency in the absence of magnetic field is \( \omega_{SO} = 2.73 \times 10^{8} \ \text{rad/sec} \) which corresponds to 43.5 MHz. When the frequency of ultrasonic waves \( \omega \) is higher than \( \omega_{SO} \) the...
screening effect becomes incomplete in consistent with the present experiments.

Considering only the optical-mode scattering we have the expression of attenuation in the transverse magnetic field:

\[ \alpha = \frac{K^2 \omega}{2v_s (\omega/\omega_s)^2 + (1 + \omega^2/\omega_D^2)^2} \]

(1)

where

\[ \omega_s = \omega_{so}/(1+\omega_c^2)^2 \]
\[ \omega_D = (1+\omega_c^2)\omega_{Do}/f \]  \,(2)

Here \( K \) is the electromechanical coupling constant, \( v_s \) is the sound velocity, \( \omega_D \) is the diffusion frequency, and \( f \) is the trapping factor. In Fig. 2 we have plotted the theoretical curve taking tentatively \( K = 0.085^5 \), \( v_s = 3.35 \times 10^5 \) cm/sec and \( f = 0.33 \).

In the case of CdS the mobility increases with lowering temperature and we have \( \mu = 2 \times 10^5 \) cm$^2$V$^{-1}$sec$^{-1}$ at \( T = 4.2 \) K$^6 \).

Because of the presence of traps, however, the carriers in the semiconducting CdS and the light-induced carriers in photoconducting CdS are trapped so that the number of carriers decreases exponentially with lowering temperature$^7$. In the sample of CdS of 12 \( \Omega \)cm at room temperature, we found at \( T = 4.2 \) K that \( \alpha(H) - \alpha(0) = \)
Magnetic Field Dependence of Ultrasonic Attenuation in Piezoelectric Semiconductors

- 0.2 ± 0.04 dB/cm at 100–300 MHz and - 0.09 ± 0.02 dB/cm at 15 MHz.

Nearly Complete Screening Case

As an example of the nearly complete screening case we take the sample of InSb at temperatures lower than 200 K, where the dielectric relaxation frequency is higher than the frequency of ultrasonic waves we have used. We cooled the sample to 66.5 K to obtain the very high mobility of carriers. The conductivity and the mobility become $\sigma = 0.66 \, \text{n}^{-1} \text{cm}^{-1}$ and $\mu = 3.19 \times 10^5 \, \text{cm}^2 \text{V}^{-1} \text{sec}^{-1}$, respectively.

The magnetic field dependence and the frequency dependence of $\alpha(H) - \alpha(0)$ are shown in Fig. 3 and 4, respectively. In contrast to the case of GaAs, the attenuation increases with increasing the magnetic field and also with increasing the frequency. If the lattice scattering (LS) or the ionized impurity scattering (IIS) is the predominant mechanism, $\omega_s$ and $\omega_D$ in eq. (1) are given, in the limit of $\omega_c \tau >> 1$, by

$$\omega_s = \omega_{so}(1.132/\omega_c^2 \tau^2), \quad \omega_D = \omega_{Do}(\omega_c^2 \tau^2/1.132), \quad (LS)$$

or

$$\omega_s = \omega_{so}(3.40/\omega_c^2 \tau^2), \quad \omega_D = \omega_{Do}(\omega_c^2 \tau^2/3.40), \quad (IIS)$$

respectively. The theoretical curves for (LS) and (IIS) are shown in Fig. 4 by taking $K = 0.027$ and $v_s = 2.286 \times 10^5$ cm/sec. The figure indicates clearly that in InSb at $T = 66.5^\circ K$ the mobility of carriers is determined by the mixed scattering of (LS) and (IIS).

The authors express their thanks to M. Kikuchi and H. Hayakawa for supplying the InSb crystal and helpful discussion.

References
Effect of Depolarization Field on the Piezoelectric Hall Voltages

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1. Introduction

If an electric field is induced in a piezoelectric semiconductor by a strain, the electric current due to this field, flowing through the semiconductor, is deflected by the accompanying magnetic field, and the Hall voltage appears. This phenomenon shall be called "Piezoelectric Hall Effect" in this paper and abbreviated as P.H.E. Arlt\(^1\)) was the first to determine by using this principle the piezoelectric constants in some III-V compound semiconductors. The present authors discuss the effect of depolarization field on the P.H.E. voltage for the determination of the piezoelectric constants.

2. Measuring Procedure

The specimen is excited mechanically by a quartz composite-bar: the three-component resonator, which is composed of two identical x-cut quartz bars and a slender pillar specimen. The resonator is driven by one of the quartz bars (driver) into longitudinal vibration, since the driver is excited by an ac signal applied to full length,
adherent electrodes. The fundamental frequency of the specimen closely matches that of the driver and of the other quartz bar (gauge). This composite-resonator resonates at the fundamental frequency of each component bar. The strain amplitude in the specimen is measured by the gauge signal which appears on (small size) electrodes at the center of the gauge bar.

The slender pillar specimen is prepared so that a piezoelectric polarization can be induced along its long axis (the z direction). The magnetic field applied to the specimen \((\mathbf{B})\) is normal to the induced piezoelectric polarization \((\mathbf{P})\). The electric field due to P.H.E. \((\mathbf{E}_H)\) is normal to both \(\mathbf{B}\) and \(\mathbf{P}\): \(\mathbf{E} = (B_x, 0, 0)\), \(\mathbf{E}_H = (0, E_y, 0)\) and \(\mathbf{P} = (0, 0, P_z)\).

3. Piezoelectric Hall Voltage

(a) Hall voltage

The observed Hall voltage is given by

\[ V_H = \int E_y \, dy \]  
(1)

where \(E_y\) is determined as follows.

The charge appearing on the Hall electrodes under \(B_x\) is given by

\[ Q_t = \oint E_y \, dA + \iint J_y \, dA \, dt \]
\[ = E_y A - \iota \sigma E_y A/\omega - \iota J_z \mu B_x A/\omega \]  
(2)

where \(A\) is the surface area of electrodes on the \(y\) faces.

\(Q_t\) can also be rewritten as

\[ Q_t = (\varepsilon_y E_y + P_y) A \]  
(3)
Piezoelectric Hall Effect

where \( P_y \) is the total polarization and \( E_y \) is the electric field in the crystal since

\[
E_y = - L_y P_y
\]

(4)

Here \( L_y \) is the depolarization factor along the y direction and

\[
\varepsilon_o = 8.85 \times 10^{-12} \text{ F/m}.
\]

From Eqs. (2) and (3),

\[
E_y = i \frac{L_y J_x B_x/\omega}{1 + L_y (\varepsilon - \varepsilon_o - i \sigma/\omega)}
\]

(5)

(b) Evaluation of the current \( J_z \) due to the piezoelectric field

It is assumed that displacement in the z direction is given by

\[
\xi(z) = \xi_0 e^{i\omega t} \sinh(\gamma z)
\]

(6)

where \( \gamma \) is a complex propagation constant and \( \omega \) is the angular frequency of excitation. The current, which has to satisfy the continuity equation, is given by

\[
J_z = - \frac{L_z d_{33} S_z}{s_{33} E [1 + L_z (\varepsilon - \varepsilon_o - i \sigma/\omega)]}
\]

(7)

where \( \varepsilon , \sigma , s_{33} , d_{33} \) and \( L_z \) are the dielectric constant, conductivity, elastic compliance, piezoelectric constant and depolarization factor in the z direction, respectively, and \( S_z \) is the strain in the specimen:

\[
S_z = \partial \xi(z)/\partial z = \gamma \xi_0 e^{i\omega t} \cosh(\gamma z)
\]

(8)

From Eqs. (5) and (7),

\[
E_y = - i \frac{L_y L_z \mu (\sigma/\omega) d_{33} B_x S_z}{[1 + L_y (\varepsilon - \varepsilon_o - i \sigma/\omega)] [1 + L_z (\varepsilon - \varepsilon_o - i \sigma/\omega)]}
\]

Since the depolarization field makes a part of the inner electric field, the magnitude of interaction between the electrical and elastic
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systems in a piezoelectric crystal, is affected by the strength of the
depolarization field in the crystal. Therefore, the electromechanical
properties\textsuperscript{2)} and the P.H.E. voltages of a specimen with a small
dielectric constant are dependent upon the depolarization factor \( L \),
in which the electrical flux leakage from the crystal is implicitly
included.

4. Experimental Results

In order to check the
measuring scheme and devices,
a highly conductive CdS crystal
was chosen as the specimen.
The Hall voltage was measured
by a lock-in amplifier (phase sensitive detector). It is made clear
from the experimental results that the emf voltage due to the vibration
of the lead-wires from the Hall electrodes in the magnetic field is
negligibly small in comparison with the voltage due to P.H.E.\textsubscript{0}, since
the Hall electrodes are located at the nodal point of the specimen.
The Hall voltage vs the magnetic field strength is shown in the figure,
from which the piezoelectric constant \( d_{33} \) is evaluated at \( 6 \times 10^{-10} \text{C/N} \).
This is about 60 times as large as \( 10.32 \times 10^{-12} \text{C/N} \), the \( d_{33} \) value
of the photoconductive CdS crystal studied by Berlincourt et al\textsuperscript{3)}.
Here the following values are used: \( \sigma = 2.6 \times 10^{3} \text{ohm}^{-1} \text{cm}^{-1} \),
\( R_{H} = \mu / \sigma = 5.6 \times 10^{-6} \text{m}^{3} / \text{C} \), \( \omega = 2 \pi \times 1.3 \times 10^{5} / \text{sec} \),
\( \varepsilon = 10 \varepsilon_{0} \), \( S_{z} = 1.6 \times 10^{-4} \), \( S_{33} = 1.7 \times 10^{-11} \text{m}^{2} / \text{N} \).

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On the Interaction between Electron Beams and Ultrasonic Surface Waves
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Introduction

In recent years, many papers have been reported on the interaction between ultrasonic waves and the carriers in semiconductors. However, the interaction between elastic surface waves and electron beams is possible. This paper considers the interaction mechanism between suitably controlled electron beams and the electric field induced by surface waves along a quartz crystal plate, by a simple model. The investigation is physically also interesting as a problem concerned with dispersion characteristics of electron beams.

Interaction mechanism

Fig. 1 shows the schematic arrangement of the interaction system, in which a quartz plate is set on anode side, and a suitable electrostatic field $E_0$ and magnetic field $B$ are applied in $y$- and $x$-direction respectively. Let electron beams be injected into the interaction space with velocity $v_e$. If the elastic surface waves propagate along the surface of the plate, the electric fields, $E$ is induced by the piezoelectric effect of quartz. Therefore, electron beams

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meander when they travel in AC electric fields. Consequently, it is expected that the ultrasonic waves are amplified under the condition \( \lambda_m > \lambda \), where \( \lambda \) is the wave length of AC electric field and \( \lambda_m \) the pitch of the meandering electron beams. As well known, the phase velocity for the cyclotron wave of electron beams, \( v_p \), is represented by \( v_p = v_e \cdot \frac{1}{1+i \omega_m/\omega} \), where \( \omega_m \) and \( \omega \) are the cyclotron and the operating ultrasonic angular frequency respectively. If \( \omega_m \gg \omega \), it takes \( v_p = (\tau \omega/\omega_m) v_e \). Therefore, by making \( \omega_m \) sufficiently larger than \( \omega \), the phase velocity of electron beams \( v_p \) approaches to that of the ultrasonic waves.

On referring to the travelling wave tube theory, the analysis is carried out by the following procedure; (1) To find the electric field induced over the surface of quartz plate by the density modulation electron beams. (2) To derive the expression of electron beams modulated by electric field due to the ultrasonic surface wave.

To simplify the calculation, we treat the surface wave like a body wave having a uniform stress distribution in the direction of depth of crystal plates. We assume that \( e^{i(\tau z + j \omega t)} \), where \( +\tau \) and \( -\tau \) correspond to backward and forward waves respectively. The AC component of electric field in the quartz plate, \( E \) is led by the ordinary piezoelectric equations as follows

\[
E = \frac{J}{\omega \varepsilon} (1 + \frac{\beta^2}{1 + \Gamma^2 + \beta^2 K^2}),
\]

where, \( K \): the electromechanical coupling coefficient, \( \beta = \omega / \nu_s \), \( \varepsilon \): dielectric constant of the crystal plate, \& \( J \): current density, \( J = -\partial D / \partial t \)

For electric field in the interaction space, we assume that

\[
E = k_0 E, \quad E = -jk_1 E.
\]

where \( k_0 \) and \( k_1 \) are proportional constants respectively.

On the other hand, in the system as shown in Fig. 1, the following equations hold

\[
\ddot{z} - \omega_m \dot{y} = \eta E_z,
\]

\[
\ddot{y} + \omega_m \dot{z} = \eta E_y,
\]
Interaction between Electron Beams and Ultrasonic Surface Waves

where \(n = -e/m, \delta y \) and \(\delta z \); AC velocity of \(y\)-and \(z\)-direction of electron beams, respectively. Eq. (3) leads the relation as

\[
(\Gamma^2 + \beta_m^2) \delta y = -\frac{n}{V} (\beta_m E_x + \Gamma E_y). \quad \ldots \quad (4)
\]

Now suppose that \(\Gamma\) nearly equals to the propagation constants of surface waves. Then we put

\[
\Gamma = \beta (j - \delta). \quad \ldots \quad (5)
\]

From the combination of Eqs. (2) and (4), the backward wave is given by the root of the equation

\[
\delta^4 + j(\alpha - 4)\delta^3 + (\gamma^2 + \delta^2 + \beta^2)\delta^2 + j(2 - 2\gamma^2 - 2\alpha - 2g\gamma + \alpha\xi^2)\delta + \alpha(1 + g\gamma)k^2 = 0. \quad \ldots \quad (6)
\]

where \(\alpha = -k_0(n\omega^2)(1/\omega\varepsilon)(1/\beta), \quad \gamma = \beta_m/\beta, \quad g = k_1/k_0\)

since \(\delta\) is a very small quantity, we ignore the terms of \(\delta^3\) and \(\delta^4\) in Eq. (6). Furthermore, the term of \(\delta\) vanishes if the magnetic flux density \(B\) is chosen in a suitable value. Then we can find easily as

\[
\delta = \pm \sqrt{\frac{a(1 + g\gamma)}{4 - 2\gamma}} \quad \ldots \quad (7)
\]

Let \(L\) stand for the length of the interaction space and \(N\) the wave number. We get, \(2\pi N = BL\). The gain of the growing wave, \(G\) can be obtained by

\[
G = 54.55 \delta N. \quad \ldots \quad (8)
\]

Our interaction analysis has been led by the use of the characteristic equation. It is, therefore, necessary to discuss whether the obtained wave is the growing or the evanescent one. According to the \(\beta-\omega\) diagram shown in Fig. 2, it is expected to be the growing wave.

Fig. 4 shows an example of calculated results for the gain under the parameters:

\[
E_0 = 2 \times 10^5 \text{ (V/m)}, \quad f = 2 \text{ MHz}, \quad V = 3.3 \times 10^3 \text{ (m/s)}, \quad \kappa = 0.1, \\
k_0 = 0.34, \quad g = k_1/k_0 = 0.3, \quad \varepsilon/\varepsilon_0 = 4.5.
\]

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![Graph 1: β-ω diagram for the growing wave.](image)

![Graph 2: Gain vs the emission current density.](image)

Experiments

Fig. 4 shows the configuration of the test tube with an M-type electron gun. A quartz plate with interdigital type electrodes as input and output terminals is mounted on the anode side. In order to apply effectively the DC electric field from the quartz surface without reducing the AC electric field of the interaction space, thin Ni-Cr film is evaporated on the quartz surface. By DC beam test, the current density to the collector, $J = 10\ mA$ is obtained. We observe the amplification of several dB by the experiments of the interaction under the suitable value of DC electric and magnetic fields.

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Generation of Even Subharmonics in a Photoconducting CdS Acoustic Amplifier

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Traveling-wave parametric amplification of even subharmonics of 1.0-GHz shear waves has been observed in photoconducting CdS at room temperature for electronic drift velocities, $v_d$, from 0.14 to 3 times the velocity of sound, $v_s$. The nonlinearity responsible for this effect is the interaction of the bunched space charge associated with one acoustic frequency with the electric field associated with another acoustic frequency. The pump had an angular range of about $\pm 4^\circ$ to the current direction. The acoustic thermal noise component at the even subharmonic served as the signal and idler.

The experimental arrangement is shown in Fig. 1. The dimensions of the sample were 5 x 1 x 1 mm with the long (current) direction oriented perpendicular to the c axis. The average resistivity of the sample went from $6 \times 10^3$ ohm-cm in the dark to $2 \times 10^3$ ohm-cm under illumination from a high-pressure Hg lamp. Resistivity variations for $v_d < v_s$ were no more than 20% over the length of the sample. The sample was placed entirely within a coaxial reentrant cavity (loaded Q = 1000) and mounted between the cavity post, held at dc ground potential and a brass electrode. Silver paste contacts were used on the unpolished ends of the sample to which negative high-voltage pulses were applied through the brass electrode.

Fig. 1. Schematic diagram of the apparatus
The cavity was excited with microwave power of 12 watts maximum, the sample serving as its own shear wave transducer. A 100-μsec microwave pulse was applied synchronously with a 100-μsec voltage pulse. The applied voltage required for \( v_d = v_s \) was taken as that voltage for which the current first decreased from its ohmic value with microwave power, \( P_{mw} \), incident on the cavity. This was 350 V, implying a mobility of 250 cm²/V-sec. For \( P_{mw} = 0 \) the kink in the current-voltage curve occurred at \( v_d = 1.3 v_s \), presumably because the small sample length limited the total flux.

The shear waves were detected by means of Brillouin scattering of a 20-mW He-Ne laser beam. A laser source chopped to produce 50-μsec light pulses was used to keep the increase in current caused by the laser light down to 2%. Detailed measurements were made for acoustic waves in the basal plane only. The frequency and propagation angle of the acoustic waves were determined by measuring \( \theta_s \) and \( \theta_1 \) (defined in Fig. 1) and applying the modified Bragg law for Brillouin scattering in anisotropic media.²

Figure 2 gives the typical drift-velocity dependence of \( P_f \) and \( P_{f/2} \) the acoustic power at the acoustic fundamental \( f \) and the subharmonic \( f/2 \) respectively, measured for on-axis waves near the cathode. Initially, \( P_f \) increases with \( v_d \), consistent with the predicted decrease in the linear electronic attenuation.⁵ Only \( P_f \) was observed in the sample for \( v_d < 0.14 v_s \). However, above \( v_d = 0.14 v_s \), \( P_f \) reaches a maximum and then falls rapidly with \( v_d \) while \( P_{f/2} \) first appears and then increases. The rise in \( P_{f/2} \) with \( v_d \) cannot be explained by linear electronic gain. If \( v_d \) were actually higher than \( v_s \) due to some local fluctuation in resistivity, then \( P_f \) would also have to increase whereas it is seen to decrease. The variation of \( P_{f/2} \) with \( v_d \) is most reasonably explained by parametric amplification, with the pump at \( f \) amplifying the signal at \( f/2 \) originating in the thermal noise. In general, the positions in the sample and acoustic propagation directions that have large \( P_f \) for \( v_d < 0.14 v_s \) show large \( P_{f/2} \) for \( v_d > 0.7 v_s \). Additional evidence for parametric amplification is given in Fig. 3 where the threshold value of

\[
1 - \frac{(v_d/v_s)}{\gamma_{th}}
\]

at a point for the onset of on-axis
$P_{f/2}$ is shown to increase with increasing microwave power. Finally, it is interesting to note that $P_{f/2}$ decreased with time, sometimes by as much as an order of magnitude over 25-μsec.

Spatial probing of the sample showed that, for $v_d > 0.14 v_s$, $P_{f/2}$ increased from zero close to the cathode, reaching a maximum near the center of the sample. For example, at $v_d \geq v_s$, $P_{f/2}$ grew 10 dB over 1 mm. The subsequent fall off of $P_{f/2}$ occurs in a region in which at $v_d = 0$, $P_f$ has diminished from its peak near the cathode due to lattice and electronic attenuation. When $v_d > 1.3 v_s$ and $P_{mw} = 0$, internally generated waves were detected which, in contrast, always peaked at the anode and had a frequency of maximum intensity below 250 MHz. With $v_d = 3.2 v_s$, the net nonparametric gain was about 140 dB/cm at 500 MHz.

In the sections of the crystal where $P_{f/2}$ becomes large, a weak $P_f$ builds up, apparently due to harmonic generation from $P_{f/2}$. When $v_d > 1.3 v_s$, even subharmonic power at $f/4$ is generated, presumably because of parametric amplification, with $P_{f/2}$ as the pump. For $v_d > 1.3 v_s$ the situation is more complicated, however, because acoustic noise for frequencies between 150-MHz and 1-GHz is observed to be amplified in the conventional nonparametric manner.

Equations have been solved describing the net parametric gain near threshold of shear waves due to a longitudinal pump. The solution to equations similar but valid for a shear wave pump is found in reference 1. It is predicted for the present case that as $v_d$ increases from zero, the electronic loss decreases while the parametric gain remains relatively constant. Assuming a subharmonic lattice loss of 5 cm$^{-1}$ and taking $\omega_c = 5 \times 10^8$ sec$^{-1}$, $\omega_D = 5 \times 10^9$ sec$^{-1}$ and $\mu \approx 250$ cm$^2$/V sec, net gain at $\gamma_{th} = 0.3$ occurs for a strain of $3 \times 10^{-5}$, which is of the same order of magnitude as obtained from rough estimates. The dotted line in Fig. 3 is the prediction for $\gamma_{th}$ versus pump power and the agreement with experiment is seen to be reasonable. Because of dispersion an angle of several degrees is needed between the pump and signal for phase matching. Unfortunately this prediction could not be experimentally checked with accuracy because the pump was not unidirectional but had an angular spread of about 8°.
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These data suggest that parametric amplification may be an important factor in the downshift in the frequencies of maximum intensity and the intensity peaking at off-axis angles observed for internally generated domains in semiconducting CdS and ZnO. 8

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Brillouin and Rayleigh Scattering of Light by Relaxing Liquids

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Introduction

Using Van Hove's density correlation function technique, the spectral intensity of light scattered by a relaxing liquid is calculated. The treatment differs from the previous work on the subject, due to Mountain,\textsuperscript{1, 2} in two respects: (a) the liquid is assumed to have a relaxing shear viscosity instead of a static shear viscosity, and (b) instead of using the time integral representation for the relaxing bulk viscosity, we consider it to arise from the relaxation of an ordering parameter and apply the thermodynamic theory of relaxation processes to calculate the correlation function. The first modification is necessary if the theory is to explain the occurrence of Brillouin components in highly viscous liquids like glycerine. The second modification gives an insight into the nature of approximations involved in using the integral representation for the bulk viscosity.

Calculation

The spectral intensity of light scattered by a liquid is proportional to the structure factor $S(k, \omega)$ which may be shown to be given by

$$S(k, \omega) = \int_{-\infty}^{\infty} e^{-i\omega t} \langle \rho(-k, t) \rho(k, t) \rangle \, dt,$$

where $\rho(k, t)$ is the Fourier component of wave-vector $k$ of the density fluctuations at time $t$, $\rho(k, \omega) \equiv \langle \rho(k, \omega) \rangle$, and the angular brackets denote the ensemble average over the initial states. $k$ is related to the scattered and incident light wave-vectors $k'$ and $k''$ by $k = k' - k''$, and $\omega$ is the difference between the scattered and incident light frequencies.
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The main problem is to calculate $\rho(k, \omega)$ in terms of an initial fluctuation $\rho(k)$. The basic equations for this purpose are the generalized form of Navier-Stokes equation to incorporate relaxing shear viscosity, the equation of continuity, the energy transport equation and the equation governing the relaxation of an ordering parameter $\xi^3$:

$$\frac{\partial \rho}{\partial t} + \rho \frac{\partial \mathbf{u}}{\partial t} = \nabla \cdot \mathbb{S} \mathbf{c} \mathbf{u} = 0, \quad \rho \frac{\partial \mathbb{S}}{\partial t} = \nabla \cdot \tau \mathbb{c} \mathbf{u} = 0, \quad \frac{\partial \xi}{\partial t} = -L \frac{\partial \xi}{\partial t},$$

where $\mathbb{S}$ is the thermodynamic variable conjugate to $\xi$, $L$ a constant or a slowly varying function of $\rho$ and $T$, and other symbols have their usual meanings. If the shear deformations relax with a single relaxation time $\tau_\omega$, $\eta(t) = \xi(t) = \frac{\xi_\infty}{1 + e^{-t/\tau_\omega}}$, where $\xi_\infty$ is the "instantaneous shear modulus" appropriate to processes occurring at frequencies such that $\omega \tau_\omega >> 1$.

Let $\rho(k, \omega)$ be the Fourier (space) and Laplace (time) transform of $[\rho(\mathbf{r}, t) - \rho_0]$ and $\rho(k)$ the Fourier transform of $[\rho(\mathbf{r}, t) - \rho_0]$, with similar notations for the transforms of $\mathbb{S}$ and $T$. Then if one takes $\rho$, $T$ and $\mathbb{S}$ as independent variables and notes that $\langle \rho(-k) \mathbb{S}(k) \rangle = 0$, one obtains from (2) that $\langle \rho(-k) \mathbb{S}(k) \rangle = \langle \rho(-k) \mathbb{S}(k) \rangle \propto \sigma(k, \omega)$ with

$$\sigma(k, \omega) = F(y) [\mathbb{S}(k \omega) y] = (\sqrt{\nu} k \mathbb{S}(k \omega) y) \left\{ \begin{array}{l}
\left[1 + \frac{1}{2} \left[ \frac{T + \mathbb{S}}{\mathbb{S}_0} \mathbb{S} \right] x_1 + \left[ \frac{T + \mathbb{S}}{\mathbb{S}_0} \mathbb{S} \right] x_2 \right] + \left[ \frac{T + \mathbb{S}}{\mathbb{S}_0} \mathbb{S} \right] \mathbb{S} \right\}
\end{array} \right.$$

where $\mathbb{S}_0 = (\mathbb{S}_0 + \frac{1}{2} \mathbb{S} \mathbb{S})^{1/2}$ is the sound velocity at zero frequency, $y = \omega/\nu k \mathbb{S}$, $\mathbb{S}_0 = (\mathbb{S}_0 + \frac{1}{2} \mathbb{S} \mathbb{S})^{1/2}$ is the sound velocity at infinite frequency and

$$\begin{array}{l}
\mathbb{S}_0 \equiv \mathbb{S}_0 k \mathbb{S} \mathbb{S} \mathbb{S}_0^{-1}, \quad \mathbb{S}_0 = \mathbb{S}_0 k \mathbb{S} \mathbb{S}_0^{-1}, \quad \mathbb{S}_0 = \mathbb{S}_0 k \mathbb{S} \mathbb{S}_0^{-1}, \quad \mathbb{S}_0 = \mathbb{S}_0 k \mathbb{S} \mathbb{S}_0^{-1}
\end{array}$$

$\mathbb{S}_0 = \mathbb{S}_0 k \mathbb{S} \mathbb{S}_0^{-1}$ is the relaxation time for $\xi$ at constant $\rho$ and $T$.$

$\sigma(k, \omega)$ is now given by $\langle \rho(-k) \mathbb{S}(k) \rangle = \sigma(k, \omega) \propto \sigma(k, \omega)$, where $\sigma(k, \omega)$ is the Fourier transform of $\sigma(k, \omega)$ which in turn is the inverse Laplace transform of $\sigma(k, \omega)$.

One readily shows that

$$\sigma(k, \omega) = \int_{-\infty}^{\infty} e^{-i\omega t} \sigma(k, \omega) dt = 2 \text{Re} \sigma(k, \omega) \propto \omega.$$

Eqn. (5), with $\sigma(k, \omega)$ given by (3), is the exact expression for $\sigma(k, \omega)$, for our model. However, the variation of $\sigma(k, \omega)$ with $\omega$ is
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more apparent from the following approximate form for $\sigma(\mathbf{k}, \omega)$:

$$
\sigma(\mathbf{k}, \omega) \approx \sum_{m=0}^{2} \frac{\beta_m \sigma_m}{\omega^2 + \beta_m^2} + \sigma_\beta \left[ \frac{2 \Gamma}{(\omega + \nu \mathbf{k})^2 + \Gamma^2} - \frac{2 \Gamma}{(\omega - \nu \mathbf{k})^2 + \Gamma^2} \right] + \frac{2 g}{(\omega + \nu \mathbf{k})^2 + \Gamma^2} - \frac{\omega - \nu \mathbf{k}}{(\omega - \nu \mathbf{k})^2 + \Gamma^2},
$$

where $-\beta_m$, $m = 0, 1, 2$, are three real roots of the equation $\mathcal{G}(\Delta) = 0$, and the remaining two roots are $-\Gamma^2 \pm \nu \mathbf{k}$, where $\nu$ can be interpreted as the velocity of sound and $\Gamma$, the absorption per second. $\sigma_m$, $\sigma_\beta$, and $g$ are constants and the consistency of the solution requires that

$$
\sum_{m=0}^{2} \sigma_m + 2 \sigma_\beta = 0, \quad 2 g \nu \mathbf{k} = \sum_{m=0}^{2} \sigma_m \beta_m + 2 \sigma_\beta \Gamma.
$$

The roots of $\mathcal{G}(\Delta) = 0$, and consequently $\sigma_m$, $\sigma_\beta$, and $g$ can be determined only approximately. Explicit expressions for them for several limiting cases of the parameters $\chi$, $\mathcal{X}$, and $\mathcal{X}_2$ are being reported elsewhere. Here we content ourselves by pointing out some of the main conclusions.

Discussion

We first observe from (6) that the central or Rayleigh component (first three terms) is a superposition of three Lorentzians, each peaked at the incident ($\omega = c$) frequency. One of these arises from the thermal conductivity and the other two from the bulk and shear relaxations. The next two terms represent the Brillouin components. The last two terms are usually small, but can be of significance either if $\Gamma$ is large, or if the intensity in the central component is small as is the case for water. The existence of these two terms in the solution which were overlooked by the previous workers has also been recently pointed out by Montrose et al.\(^4\).

We next note that usually $\chi \ll 1$, and consider first the case $\chi_2 \ll \varpi_0^\infty$. Mountain formulated the problem essentially for this case and in agreement with his main result we find that the central component now consists of only two Lorentzians—one due to thermal conductivity and the other due to bulk relaxation. However, our expression for $\sigma(\mathbf{k}, \omega)$ becomes identical with his only if the relaxation process giving rise to bulk viscosity is such that $\xi = \xi^\infty$, or equivalently if $\beta_0 - \beta_2 = \beta_0^\infty - \beta_2$, i.e., if the relaxation is induced by fluctuations in density alone (and not those in temperature). As is to be expected, the difference between the results obtained by the two treatments (thermodynamic versus time integral representation of bulk viscosity) is found to be small when $\chi \ll 1$, but not so when $\chi_2 \ll 1$.\(^4\)
Finally if both $\chi_1$ and $\chi_2 \gtrless 1$, then all the three Lorentzians contributing to the central component have comparable intensities. This case is relevant to viscous liquids where by lowering the temperature one can span the whole range of values from $\chi_1, \chi_2 \ll 1$ to $\chi_1, \chi_2 \gg 1$. One finds that the Brillouin components should become less and less pronounced as the temperature is lowered ($\chi_1, \chi_2$ increased), which is in agreement with the observed temperature variation of $\tau(k, \omega)$ in glycerine$^{5,6}$. For $\chi_1, \chi_2 \ll 1$, the ratio of the integrated intensity in the central component to that in the Brillouin components is given by the Landau Placzek value: $I_L/(2 I_Q) = \chi^- 1$, where as at the other limit, $\chi_1, \chi_2 \gg 1$, $I_L/(2 I_Q) = \chi^2 \chi^2/\chi^2 - 1$. We note that if we had considered a non-relaxing (frequency independent) shear viscosity, i.e. had written for the integral in eqn. (2) just $\gamma \text{ grad div } \mathbf{u}$, where $\gamma = \mathbf{G} / \mathbf{G}$, is the ordinary shear viscosity, then, as may be readily shown, the expression for $\tau(k, \omega)$ would have contained no Brillouin peaks for $\chi_2 > \frac{3}{2} B_S / G$.

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Brillouin Scattering Spectrometer

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1. Introduction: With the development of laser systems, the study of the fine structure in the Rayleigh line during the process of molecular scattering of light has been used to determine the sound-velocity and the sound-absorption coefficient in the gigacycle-per-second region. Light scattering techniques permit a study of velocity dispersion and excess absorption, associated with thermal and/or structural relaxation effects in transparent liquids, beyond the present limits of ultrasonic investigations. For structural relaxation in viscous liquids it is possible to cover a substantial portion of the dispersion region with light scattering techniques by a temperature variation of the liquid under study. To investigate thermal relaxation in nonviscous organic liquids, where the temperature range of the liquid state is limited, a substantial portion of the dispersion region can be investigated only by wide variation of the scattering angle. The theoretical analysis of the frequency spectrum of scattered light due to density fluctuations within relaxing and nonrelaxing liquids is treated in detail elsewhere.\(^{(1)}\)

This paper will describe a variable angle spectrometer to be used in the study of thermal relaxation processes in dispersive liquids by measuring the frequency dependent shift and line width of the Brillouin doublet.\(^{(2)}\)

The following two papers contain up-to-date references for the theoretical and experimental treatment of Brillouin scattering in relaxing and nonrelaxing liquids:

Brillouin Scattering Spectrometer

2. Description of Scattering System:

A schematic representation of the Brillouin Scattering Spectrometer is shown in following figure:

A. Source: A temperature-controlled, frequency-stable, source of coherent radiation is provided by a helium-neon gas laser operating in a single mode with a radiation output of about 300 microwatts at 6328 A.U. An automatic servo-control, a piezoelectric element on which is mounted one of the resonator mirrors, provides long-term wavelength stability. A collimating telescope attached to the laser aperture provides focusing of the output beam at the center of the scattering cell. The laser system is mounted on an arm that is free to rotate through 180° about the scattering cell. Independent vernier-controls provide for alignment of the laser system with facets of scattering cell by autocollimation.

B. Scattering Cell: In order to permit light scattering measurements to be made over a substantial portion of the region of thermal relaxation in dispersive liquids, a special scattering cell was constructed. Most experimental studies to date of Brillouin scattering have been made at a fixed scattering angle, usually 90°. Rectangular optical cells with this configuration have the desired precision. With the alignment of laser source and detector, relative to the optical scattering cell, by means of autocollimation the scattering angle is known with sufficient precision. With cylindrical or spherical scattering cells however, due to the need of focusing and collecting lens systems as well as the absence of optically flat surfaces for above alignment, a significant uncertainty in the scattering angle is present. For an uncertainty of ± 1 degree in the scattering angle the following uncertainties are introduced in velocity measurements at the angles indicated: 30° (+7%), 60° (+3%), 90° (+2%), 150° (+5%). Preliminary results show that for many dispersive liquids the entire thermal relaxation region to be studied lies within scattering angles from 0° to 90°. The velocity change in the dispersion region is of the order of magnitude of 12 to 15 percent. Scattering angles have to be known to at
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least ± 0.1% for reliable velocity measurements.

The scattering cell, constructed from a rectangular block of optically perfect glass, was ground into a hollow cylinder: 5 cm in height, 20 cm in outer diameter, with a wall thickness of 1 cm. Optically flat facets were ground and polished on the outer surface of the cell at 5° intervals between 0° and 180°. The surfaces are flat to λ/4 and the angles between surfaces are known to better than 0.01°. The scattering cell is mounted on a "heat sink" which maintains temperature control in the scattering liquid to ± 0.1 °C by means of an external thermostatic circulator. The laser beam is aligned perpendicular to a given facet by autocollimation. The detecting system, aligned previously in similar manner, remains permanently fixed. Due to close matching of the indices of refraction of the glass cell wall and the dispersive liquids under study, as also the small diameter of the laser beam (less than 1 mm), corrections for the small curvature of the inner surface of the scattering cell are negligible and can be ignored.

The cell cover is designed to permit the liquid sample in the scattering cell to be prepared by slow distillation from a spectroscopic quality reagent external to the cell to reduce parasitic scattering by particulate matter. Provision is also made for locating the geometric center of the cell for preliminary adjustment and alignment of the scattering system. A thermometer used to measure the temperature of the liquid sample is mounted in the cell cover.

C. Collecting System: Scattered radiation is collected by a 50 mm, f/2 Carl Zeiss Sonar lens with a variable slit mounted on the lens to limit angular acceptance in the sagittal plane. Full aperture of the lens is used in the tangential plane. The collected radiation is focused onto a variable analyzing pinhole. A second collimating lens, with a focal length of 200 mm and the analyzing pinhole located in its focal plane, is used to illuminate a Fabry-Perot etalon with parallel light. The location of the analyzing pinhole, different from conventional procedures, is deemed critical for optical alignment of detecting system relative to the scattering cell. In addition, the maximum diameter of the pinhole is determined by the conditions of angular source extension to permit only the first angular fringe to illuminate the Fabry-Perot etalon.

D. Analyzer: The scattered radiation is analyzed by a linear pressure-scanned Fabry-Perot etalon. The fixed spacing in the etalon can be varied in 2 mm steps from 2 mm to 100 mm. The interferometer plates have an effective aperture of 45 mm with a flatness of 1/120 λ over the working surface at 6328 A.U. The plates are coated with a dielectric film whose reflection coefficient is 0.95 at
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6328 A. U. Under these conditions the interferometer has a figure and reflection finesse of about 60. To increase the effective finesse of the analyzing system variable irises are mounted both before and after the interferometer.

E. Detecting and Recording System: An EMI-9558-A photomultiplier tube, cooled to dry-ice temperatures, is illuminated by parallel light from the Fabry-Perot etalon over the entire photosensitive surface. No condensing lens and analyzing pinhole is used in front of the photomultiplier tube. Because of the weak scattering signal associated with the single mode laser, photon-counting techniques are used to detect and record the analyzed scattered radiation.

F. Linewidth and Instrument Broadening: The displacement (4.25 - 5.00 Gc) and corresponding linewidth (0.05 - 0.55 Gc) of the phonon mode relative to the thermal mode (\(\sim 40\) Mc) provides data for acoustic velocity and sound absorption coefficient in liquids. To evaluate experimental results it is necessary to determine the effect of broadening and distortion of the intensity profile of the frequency spectrum of scattered radiation. We have an experimental problem of double resolution smearing: one due to Doppler broadening of laser line shape; the other associated with instrument broadening by Fabry-Perot etalon and resolution broadening by analyzing pinhole. Asymmetry can be introduced into line shape of the phonon mode due to presence of coupling mode associated with relaxation processes as well as overlap of the phonon mode with adjacent thermal and phonon modes.

Doppler broadening of multimode laser linewidth (1500 Mc) is avoided by using single mode laser line (\(\sim 0.01\) Mc). Selection of diameter of analyzing pinhole (< .5 mm) so that fraction of fringe order viewed at pinhole is of the order of flatness of plates (\(\sim \lambda/100\)) of Fabry-Perot etalon reduces to a minimum its contribution to resolution broadening. Apparatus half-width of etalon described above is given by 0.245/t, (Gc) where t is value of etalon spacer in cm. The experimental lineshape results from a convolution of the true lineshape with that of the Fabry-Perot etalon. To minimize instrument broadening, as also corrections for overlap of thermal and phonon spectral lines, the etalon spacer is selected so that the free spectral range (15.02/t, Gc) is approximately three times the frequency displacement of the thermal and adjacent phonon mode.
Interaction of hypersound and high-intensity light

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The photoelastic coupling of elastic waves and intense laser light leads to the stimulated Brillouin-Mandelstam light scattering observed in a number of gases, liquids and solids. In solids under certain condition a simultaneous stimulated scattering on the longitudinal and transversal elastic waves has been observed in [1]. In the present paper the light intensity threshold for exitation of transverse elastic waves will be estimated.

The phenomenological equations describing the photoelastic coupling between electromagnetic and elastic waves are the Maxwell's equations with dielectric constant dependent of the elastic deformation and the elastic equations with the electrostrictive force taken into account. The intense light wave with frequency $\omega_s$, wave vector $\vec{k}_s$ and electric-field amplitude $\vec{E}_s$ propagated in solid will be scattered on the elastic vibration of the lattice. According to the Bragg condition the most effective scattering will take place in the case when elastic wave propagate in the same direction as the light wave and the scattered waves (Stoces waves) are observed in the opposite direction. In the solid there exist two elastic waves with frequencies $\Omega_\varepsilon = q \nu_\varepsilon$ and $\Omega_\perp = q \nu_\perp$ where $\nu_\varepsilon$ and $\nu_\perp$ velocities
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do longitudinal and transvers elastic waves respectively and \( \mathbf{q} \) is their wave vector, which is equal \( \mathbf{q} = 2 \mathbf{\kappa}_0 \). The phase matching condition are

\[
\omega_1 = \omega_0 - \Omega_\epsilon, \quad \omega_2 = \omega_0 - \Omega_\epsilon
\]

\[
\mathbf{k}_1 = \mathbf{q} - \mathbf{\kappa}_0, \quad \mathbf{k}_2 = \mathbf{q} - \mathbf{\kappa}_0 + \Delta \mathbf{\kappa}
\]

where \( \omega_1, \omega_2 \) are frequencies and \( \mathbf{k}_1, \mathbf{k}_2 \) - wave vectors of two Stoces waves, scattered on the longitudinal and trasvers elastic wave respectively; \( \Delta \mathbf{\kappa} = q \eta \mathbf{u}_c - \mathbf{U}_c \) with \( \eta \) - the refractive index and \( c \) - light velocity in vacuum. Assuming that the laser light wave linearly polarised in the \( x \) direction propagate in an isotropic solid along the \( z \) direction and that the amplitudes of displacement in elastic waves \( \mathbf{u}_e \) and \( \mathbf{U}_e \) and the amplitudes of reflected light waves \( \mathbf{E}_1 \) and \( \mathbf{E}_2 \) are slowly varying functions of the distance, we obtain the equations for amplitudes of waves satisfying the condition (1) in the form

\[
\frac{d\mathbf{E}_1}{dz} + \mathbf{q} \cdot \omega_1 \mathbf{u}_e \mathbf{E}_{ox} \mathbf{E}^*_{ox} = 0
\]

\[
\frac{d\mathbf{u}_e}{dz} + \mathbf{\alpha}_e \mathbf{u}_e - \frac{\varepsilon_0 + a_2}{2\pi (k + \frac{q}{3} \rho)} \mathbf{E}_{ox} \mathbf{E}^*_{ox} = 0
\]

\[
\frac{d\mathbf{E}_2}{dz} + \mathbf{q} \cdot \omega_2 \mathbf{u}_e \mathbf{E}_{ox} \mathbf{E}^*_{ox} e^{-i\Delta k z} = 0
\]

\[
\frac{d\mathbf{u}_e}{dz} + \mathbf{\alpha}_e \mathbf{u}_e + \frac{2\varepsilon_0 - a_2}{4\pi} \mathbf{q} \cdot \mathbf{E}_{ox} \mathbf{E}^*_{ox} e^{-i\Delta k z}
\]

\[
\frac{d\mathbf{E}_{ox}}{dz} + \mathbf{q} \cdot \omega_2 \mathbf{u}_e \mathbf{E}_{ax} + \mathbf{\alpha}_e \mathbf{u}_e \mathbf{E}_{az} e^{i\Delta k z} = 0
\]

where \( k \) and \( \mu \) are elastic constants, \( a_1 \) and \( a_2 \) photoelastic constants, \( \alpha_e \) and \( \alpha_e \) absorption coefficients for the longitudinal and transvers elastic waves. We suppose here that light absorption is much smaller than the sound absorption. Assuming the pump field amplitude \( \mathbf{E}_{ox} \) to be constant and cancelling the equation (6) we can obtain the condition under which the amplitudes of elastic waves
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increase with distance. For threshold intensities we obtain

\[
|E_0|^2 < \frac{2\pi (K + \frac{3}{2} \rho \mathcal{E}_0 \alpha^z)}{q \mathcal{K}_s \alpha_z (\mathcal{E}_s + \alpha_s)} \tag{7}
\]

\[
|E_0|^2 > \frac{8\pi \mu \mathcal{E}_0 \alpha^z}{q \mathcal{K}_s \alpha_s (2\mathcal{E}_s - \alpha_s)} \tag{8}
\]

Similar inequality has been obtained for quartz [2]. The numerical estimation for quartz shows that for transvers wave polarized in the same direction as the incident light wave, the threshold intensity is of the same order of magnitude as for longitudinal wave. But for the transvers wave polarized in a normal direction the threshold intensity is much larger. Thus for some correlation of parameters the simultaneous exitation of longitudinal and transvers elastic waves observed in [1] can be explained.

In the case of stimulated Brillouin–Mandelstam scattering the amplitude of sound increases exponentially with distance. When the sound amplitude is sufficiently large the nonlinear phenomena can be of importance [3]. Now the acoustic nonlinearity in the case of such amplification of sound by the action of laser light will be considered. Let us consider the longitudinal elastic wave with the displacement

\[
U_\xi = U_1 + \xi \tag{9}
\]

where \(U_\xi = \xi \mathcal{Q}_0 \cos (\Omega_0 t - q x)\), \(\mathcal{Q}_0\) - is the gain coefficient and \(U_2\) is a solution to the elastic equation in the second order approximation

\[
\frac{\partial^2 U_2}{\partial t^2} - \frac{\mathcal{Q}_0^2}{\rho_0} \frac{\partial^2 U_2}{\partial Z^2} - \frac{\eta}{2 \rho_0} \frac{\partial}{\partial Z} \left( \frac{\partial U_2}{\partial Z} \right)^2 = \frac{\beta}{2 \rho_0} \frac{\partial}{\partial Z} \left( \frac{\partial U_2}{\partial Z} \right)^2 \tag{10}
\]

where \(\rho_0\) and \(\beta\) are density and nonlinear parameter of the medium, \(\eta\) viscosity coefficient. The solution of equation (10) is equal

\[
U_2 = \frac{U_0^2 q_0^2 \beta}{\alpha^2 \rho_0^2 (s + 2d_0^2)} \left( e^{\frac{2\xi}{\mathcal{E}_0 \alpha^z}} - e^{-\frac{2\xi}{\mathcal{E}_0 \alpha^z}} \right) \cos (\Omega_0 t - q x) \tag{11}
\]
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The distance \( z_o \), where \( u_z = \frac{1}{2} u_1 \), can be formally determined. It is equal

\[
  z_o = \frac{1}{8} \ell n \left( \frac{8 \nu \delta}{u_0 \gamma^2 \rho} \right)
\]

(12)

For distances \( z \geq z_o \) the sound waves is strongly distorted because of nonlinearity and on this distances the sound wave becomes a periodic shock wave. The absorption of such wave is amplitude dependent and is much larger then the absorption of small-amplitude sound wave \([3]\). The estimation of distance \( z_o \) for quartz at room temperatures has been made. If the frequency of sound is \( f = 2,4 \times 10^6 \) \( \text{c} \text{m}^{-1} \) and the electric field amplitude \( E_o = 10^5 \) \( \text{c} \text{m}^{-1} \), then \( z_o \approx 3 \times 10^{-9} \) \( \text{c} \text{m}^{-1} \). And if the sound wave is amplified from thermal noise \((u_o \approx 10^{-18} \text{c} \text{m})\) then \( z_o \approx 3 \times 10^{-9} \) \( \text{c} \text{m}^{-1} \). For usual condition this value is smaller or of the same order of magnitude as the length of interaction between the light and sound waves. Then the acoustic nonlinear effects must be important in the sound propagation.

The generation of second harmonic in sound wave under the action of laser light has been observed in \([4]\).

References

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On Acoustic Modes and the Thermal Scattering of Light.

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The essential problem in the scattering of light by thermal fluctuations in a fluid is to calculate the intensity $I_s$ scattered through an angle $\phi$ from a monochromatic parallel beam of intensity $I_0$ and wave vector $k_0$. The Bragg condition for constructive interference selects a spatial Fourier component of the fluctuations of wave vector $k = 2k_0 \sin \phi / 2$. The temporal fluctuation of this component determines the spectrum of the scattered light. The problem reduces therefore to one of understanding the dynamics of the $k$'th spatial Fourier component (KSFC) of the fluctuations, which is best achieved through a solution to the Navier-Stokes equations of fluid dynamics for a fixed (real) value of $k$ and complex frequency $\omega$, i.e., a solution for an acoustic standing wave.

Such a solution apparently has not been available although solutions for progressive waves ($\omega$ real, $k$ complex) have been known for many years. As a result the classical theory of light scattering has had to rely on a split foundation: the frequency shift and broadening of the Brillouin components of scattered light, for example, are predicted from the acoustic nature of the KSFC, while the integrated (over $\omega$) intensities of both Brillouin and central components are predicted from the thermodynamic theory of fluctuations. Such a split is of course acceptable if the theory is internally consistent. It does not seem to have been appreciated during the half century of its use that the density and temperature fluctuations cannot be
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both (a) statistically independent, as required by the thermodynamic theory of fluctuations, and (b) explicitly related, as required by the assumption of acoustic character.

In seeking a more consistent theory of light scattering we have examined the standing wave solutions to the Navier-Stokes equations in the plane-wave acoustic approximation, including as loss mechanisms only a thermal conductivity and Newtonian viscosity. Our procedure parallels that of Truesdell for progressive wave solutions (J. Rational Mech. 2, 643, 1953). The variables are the particle velocity \( u \), and the small deviations \( \rho \) of density, and \( T \) of temperature from equilibrium. The dependence of each variable on \( x \) and \( t \) is assumed to be of the form

\[
\rho(t) = R e^{s t - j k x}
\]

with \( k \) real and \( s = a + j \omega \) complex.

The characteristic equation is found to be a cubic in \( s \) with one real root, and a complex conjugate pair for the range of \( k \) of interest. The conjugate pair defines a solution with oscillatory decay which applies to the normal acoustic standing wave, and the real root defines a solution with exponential decay which applies to a standing "temperature" wave. In general both solutions involve all fluid variables. Alternatively the fluid in motion as described by Eq. (1) may be regarded as a dynamical system with two degrees of freedom; the normal coordinates do not in general coincide with the fluid variables.

To apply the fluctuation-dissipation theorem in a familiar manner the problem in fluid dynamics is translated into circuit language. The behaviour of fluid variables \( \rho(t) \) and \( T(t) \) in the above solutions for a given value of \( k \) can be shown to be exactly equivalent to that of the free decay of the voltages \( V \) and \( V_t \) in the circuit shown in Fig. 1. The fluctuation-dissipation theorem in circuit language is Nyquist's theorem. A noise voltage generator, whose mean square output per cycle is given by \( 4 k_b T R \), is placed in series with each resistor \( R \) in accordance with this familiar theorem, and the RMS noise voltages \( V \) and \( V_t \) (and hence also \( \rho \) and \( T(t) \)) calculated by normal circuit theory.
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Fig. 1 Equivalent circuit for thermodynamic parameters in the fluid.

In light scattering $\delta n^2$, the mean square fluctuation of the index of refraction $n$ (or more precisely the KSFC of the fluctuation in that index) is of interest, since $I_s/I_o \propto \delta n^2$. Since $n = n(\rho, t)$ the fluctuation from a given source $A$ is given by

$$\delta n_A = \left(\frac{\partial n}{\partial \rho}\right)_T \delta \rho_A + \left(\frac{\partial n}{\partial T}\right)_\rho \delta T_A$$

This equation means, in terms of the equivalent circuit, that a given noise generator $A$ provides contributions to $V_\rho$ and $V_T$, and therefore also to $\delta n$, which are correlated, and therefore must be added vectorially. Since the noise output of the other generator $B$ is not correlated with that of $A$, however, their individual contributions must be added as the square, making

$$\frac{I_s}{I_o} \propto \delta n^2 = \left[\left(\frac{\partial n}{\partial \rho}\right)_T \delta \rho_A + \left(\frac{\partial n}{\partial T}\right)_\rho \delta T_A\right]^2 + \left[\left(\frac{\partial n}{\partial \rho}\right)_T \delta \rho_B + \left(\frac{\partial n}{\partial T}\right)_\rho \delta T_B\right]^2$$

(2)

Alternatively, we may say in the language of normal modes that the statistically independent fluctuation along each normal coordinate provides a correlated contribution to the fluctuation of each fluid variable. Only if the normal coordinates coincide with variables $\rho_1$ and $T_1$ do the fluctuations $\delta \rho$ and $\delta T$ become statistically independent and does Eq. (2) reduce to the classical equation

$$\frac{I_s}{I_o} \propto \left(\frac{\partial n}{\partial \rho}\right)_T^2 \delta \rho^2 + \left(\frac{\partial n}{\partial T}\right)_\rho^2 \delta T^2$$

(3)

usually attributed to Einstein and Smoluchowski.

Formulae for the spectra of the density and temperature fluctuations as well as scattered light have been calculated from the equivalent circuit and Eq. (3), but
On Acoustic Modes and the Thermal Scattering of Light.

ey are rather too bulky to record here. Comparison with the formulae of classical theory reveals a number of differences, the more significant of which have to do with the contribution from temperature fluctuations. For a liquid the $\delta T$ term in Eq. (3) is typically $1\%$ of the $\delta \rho$ term. As a result the contribution of temperature fluctuations has traditionally been neglected in the comparison of measurements of light scattering with theory. Neglect of the $\delta T$ terms in Eq. (2) however can easily result in an error of $20\%$ in the contribution from a given source for a typical liquid.

An interesting question is the reason for the failure of the thermodynamic theory of fluctuations to apply to the KSF of the fluctuations in a fluid. A condition for the validity of this theory is that all relaxation processes have characteristic frequencies much greater than the frequency range of interest, which is $0$ to $10^{10}$ Hz for the scattering of light. The circuit in Fig. 1, however, is that of a simple resonator whose compressibility relaxes from isothermal for $\omega < < \tau^{-1}$, to adiabatic for $\omega >> \tau^{-1}$, where $\tau^{-1} = \frac{\lambda k^2}{\rho_0 c_v} = 10^7$ Hz. This is a familiar type of behaviour for thermal relaxation in the confined space of a resonator, for example in a vibrating reed. Previously, however, it has been assumed (erroneously) that the thermal relaxation in a standing wave would be from adiabatic behaviour for $\omega < < \omega_r$ to isothermal for $\omega >> \omega_r$, with $\omega_r = 10^{14}$ c/s, as in a progressive wave.
Einleitung


Grundlage

Die zeitlichen Mittelwerte der mechanischen Spannungen \( \overline{T_e} \) und \( \overline{T_m} \) an der Kugeloberfläche infolge des elektrischen bzw. magnetischen Wechselseitfeldes \( \vec{E} \) bzw. \( \vec{H} \) sind bestimmt durch die Beträge (im Gauß'schen Maßsystem):

\[
\overline{T_e} = \frac{\varepsilon_0}{8\pi} \vec{E}^2 \quad \text{und} \quad \overline{T_m} = \frac{\mu_0}{8\pi} \vec{H}^2
\]

und die Regel, daß die jeweilige Feldstärke \( \vec{E} \) bzw. \( \vec{H} \) den Winkel zwischen dem Spannungsvektor und dem Normalenvektor der Oberfläche halbiert.
Unter Verwendung der Formeln für die Streufelder an Kugeln[1] und der Kugelkoordinaten $r, \vartheta, \varphi$ (siehe Figur 1) kann man die Oberflächenverteilung der Spannungskomponenten $T_r, T_\vartheta, T_\varphi$ darstellen durch

\[
T_r (\vartheta, \varphi) = \cos^2 \vartheta \cdot T_r (0, \varphi) + \sin^2 \vartheta \cdot T_r (\frac{\pi}{2}, \varphi)
\]

\[
T_\vartheta (\vartheta, \varphi) = \cos^2 \vartheta \cdot T_\vartheta (0, \varphi) + \sin^2 \vartheta \cdot T_\vartheta (\frac{\pi}{2}, \varphi)
\]

\[
T_\varphi (\vartheta, \varphi) = \sin^2 \vartheta \cdot T_\varphi (\frac{\pi}{2}, \varphi)
\]

i.h. durch die Spannungen entlang bevorzugter Meridiane. Diese selbst wurden aus den Debye'schen Streufeldreihen berechnet.

**Diskussion der Ergebnisse**

In den gezeigten Beispielen sind die mechanischen Spannungen durch Division mit der Energiedichte der ebenen Welle dimensionslos gemacht. Frequenzparameter ist $K_a = 2 \frac{a}{\lambda} \pi$ (a ist Kugelradius).

Fig. 2 zeigt den normierten Strahlungsdruck $T_Z$ in Ausbreitungserichtung, einmal für eine verlustlose Kugel ($\sigma = 0$), zum andern mit endlicher Leitfähigkeit $\sigma$. Ohne Verluste entstehen ausgeprägte Resonanzen, die den Resonanzen des elektromagnetischen Feldes im Innern der Kugel und an ihrer Oberfläche entsprechen.

Bei der Frequenz der ersten Resonanz ($K_a = 0,96$) ist in Fig. 3 die Spannungsverteilung dargestellt. Sie würde eine verformbare Kugel zu einem Ellipsoid abflachen. Bei tieferen Frequenzen bleibt diese Verteilung im wesentlichen erhalten, lediglich nimmt die Symmetrie zwischen Licht- und Schattenseite zu, so daß der axiale Strahlungsdruck abnimmt. Überhaupt ist diese Symmetrie zwischen Vorder- und Rückseite der Kugel in erster Linie verantwortlich für den Abfall des Strahlungsdrucks zu tiefen Frequenzen. Deshalb liegen hier in der Regel die mechanischen Oberflächenspannungen um Größenordnungen über dem Strahlungsdruck.
Mit wachsender Frequenz $k__a$ wird die Spannungsverteilung an der Oberfläche komplizierter. Fig. 4 ist ein Beispiel in der 3. Resonanz von Fig. 2 bei $k_a = 1,68$.

In diesem Frequenzbereich niedriger Resonanzordnung ($k_a$ etwa zwischen 1 und 5) würden verformbare Kugeln zu toroidalen Gebilden deformiert.

Erst bei relativ hohen Frequenzen ($k_a$ etwa 10) überwiegen die Spannungen an der Lichtseite deutlich die Spannungen im Schatten. Erst dann "drückt" das Licht, während es bei kleineren $k_a$ fast ebenso stark im Schatten angreift.

Die Rechnung zeigt ferner, daß durch elektrische oder magnetische Verluste zwar der Strahlungsdruck stark verändert wird (glatter Frequenzverlauf), die Verteilung der Oberflächenspannungen wird weit weniger beeinflußt. Am stärksten machen sich dielektrische Verluste bei den radialen Spannungen bemerkbar, die in der Ebene des $\vec{E}$-Vektors liegen.

Eine einfache Überschlagsrechnung zeigt an Hand der numerischen Ergebnisse, daß vor Radarantennen mechanische Spannungen am Schädel angreifen, die über der Hörschwelle liegen können und daß im Fokus von Riesenpuls lasern Spannungen von mehreren Atmosphären auftreten können.

MECHANICAL TENSIONS IN AN ELECTROMAGNETIC FIELD

Fig. 1

Fig. 2

Fig. 3

Fig. 4
Theory of the Diffraction of Light by Ultrasonic Waves:

A Successive Diffraction Computation

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1. Present state of the correspondence between theory and experiments

Although there are many works on the diffraction of light by ultrasound, the correspondence between theory and experiments remains rather poor as regards the intensity distribution of light amongst various diffraction orders. Here we restrict our consideration to the case of the normal incidence of light on plane progressive ultrasonic beam of uniform thickness in the direction of the incident light. Theoretically the independent variables pertaining to this phenomenon are three:

\[ \alpha = \lambda' / \lambda = \lambda / \lambda_0, \quad \beta = \pi L / \lambda, \quad \gamma = \delta n_o / n_0 \]  \hspace{1cm} (1)

where \( \lambda \) is the ultrasonic wavelength, \( L \) the width of the ultrasonic beam in the direction of the incident light, \( \lambda \) and \( \lambda' \) are the wavelength of light in vacuum and in the medium respectively, \( n_0 \) is the refractive index of the medium and \( \delta n_0 \) the amplitude of variation of \( n_0 \) in the ultrasonic beam. The existing theories, however, usually employ two (or one) out of the following four parameters.

\[ D = \frac{\pi L \lambda}{\lambda_0 \lambda'}, \quad \theta = \frac{\delta n_0 \lambda}{\lambda^2}, \quad v = \frac{2 \pi \delta n_0 L}{\lambda}, \quad \text{and} \quad \frac{\delta}{\lambda} = \frac{2 \pi \delta n_0}{\lambda^2} L \]  \hspace{1cm} (2)

These parameters are related to \( \alpha, \beta \) and \( \gamma \) by

\[ D = \alpha / \beta, \quad \theta = \gamma / \alpha, \quad v = 2 \beta / \alpha \]  \hspace{1cm} (3)

and there being two relations

\[ v = 2D \theta \]  \hspace{1cm} (4)

among these four parameters, independent variables are two, \( \alpha \) being usually assumed to be sufficiently small as to be omitted against unity.

Fig. 1 illustrates on a diagram with \( \log \theta \) as abscissa and \( \log v \) as ordinate, the correspondence between the theory and experiments. Of the existing exact theories (1)-(4), only that of Extermann and Wanner(1) gives concrete results to be compared with experiments. This computation, however, is performed at constant and discrete values of \( \theta (= 1, 3 \text{ and } 10) \) and with \( D \) (and therefore also \( v \)) as variable, while the experiments are usually performed at constant \( D \), so that theory and experiments are not directly comparable.

Two limiting approximations are available, the phase-lattice theory (5) and the geometrical-optical theory (6)-(9). Especially, the former gives the light intensity in terms of a single parameter \( v \) and in good approximation within certain limits of the parameters (1), (10), (11).

\[ D \leq 1, \quad Dv \leq 1, \quad v \leq \frac{c}{c_0} \leq 1 \]  \hspace{1cm} (5)

This corresponds to the area bounded by shaded line segments in Fig. 1. Here the second condition is made somewhat more severe than the original indications, considering of the fact that the rays of light converge to make focal lines at
\( \xi = 1.7 \), according to the geometrical-optical theory(6), (7).

Experiments confirming the phase-lattice theory are mainly those of Sanders(12) and Nomoto(13), while the Klein-Hiedemann experiment (14) extends far beyond the limit of applicability of this theory. Nomoto-Negishi experiment (15) extending to high value of \( \theta \) (>500) is for saw-toothed waves produced by finite-amplitude distortion, and, though not directly comparable with the Raman-Nagendra Nath theory for this reason, proved to be in fairly good agreement with the modification of the phase-lattice theory for saw-toothed waves (15), (16). It must be mentioned by the way that the phase-lattice theory is also valid for oblique incidence as regards the variation of the parameter \( \nu \) in dependence on the angle of incidence (Nomoto(17)). We use these facts, the validity of the phase-lattice theory under certain conditions for normal incidence as well as for oblique incidence, as the basis of our successive diffraction computation to be described below.

Recently, some successive diffraction computations are performed by Berry(18) using analog computer, and by Hance(19) and Hargrove(20) employing digital computers. Hargrove and Berry also explained Klein-Hiedemann experiments. In other respects, also these computations are all performed for constant values of \( \theta \) as indicated in Fig. 1. Our treatment to be described below, though independently planned and somewhat different, is along similar lines with those of Hargrove and Hance. The computation, however, covers wider ranges of the parameters, and especially extends to higher values of \( \theta \) than hitherto obtained.


We consider the ultrasonic beam of total thickness \( L^s \) to be composed of \( j=1, 2, 3, \ldots \) sub-beams or layers of thickness \( L \) each, and consider the successive diffraction of light by these sub-beams (Fig. 2). The parameters \( D, v, \) and \( \xi \) for \( L^s=jL \) are denoted by \( D^s, v^s, \) and \( \xi^s \), respectively.

While passing the first sub-beam, only the incident light (0-order) is present according to the phase-lattice theory, and various order diffraction spectra, or plane waves, with amplitudes \( A_s^s \) and phase \( \varphi_s^s \)

\[
A_s = J_s(v), \quad \varphi_s^s = 0 \quad (s = 0, \pm 1, \pm 2, \ldots)
\]  

are produced at the plane of emergence of light from the first sub-beam. The sign of spectra are positive for those spectra bent in the direction of the propagation direction of ultrasound as compared to the incident light. Negative sign of \( A_s \) occur-
ring for certain values of \( s \) and \( v \) is admitted. (Physically it means the reversal of phase.) Diffraction spectra are the Fourier components of the corrugated wavefront of Fig. 3, produced by crossing the ultrasonic beam, and point \( B \) corresponds (for normal incidence) to the point where all the diffraction spectra pass this point in phase, the convention of sign of \( A_s \) being admitted. So we have diffraction spectra with amplitudes \( A_s \) and phase zero at the plane of emergence from the first sub-beam.

Now consider the \( s \)-th order diffraction spectrum — as observed from outside—propagating in the \((s+1)\)-th sub-beam. It is composed of many components, produced from the light incident on the \( j \)-th sub-beam as the \( p \)-th order and diffracted in this layer as the \((s-p)\)-th order spectrum, where \( p = 0, \pm 1, \pm 2, \ldots \). We call these components the \((p, s)\)-components and add all these components belonging to the common order \( s \) at the plane of emergence from the \( j \)-th sub-beam, considering of the phase and amplitude. In Fig. 2, \( BE \) is the \((0,s)\)-component and \( B'B' \) is one such \((p,s)\)-component.

In case of oblique incidence under angle of incidence \( \theta' \), the phase-lattice parameter becomes as

\[
v' = v \sec \theta' \sin \left( \frac{\beta \tan \theta'}{\beta' \tan \theta'} \right)
\]

where \( \beta \) is defined in (1). So the effective value of \( v \) for oblique incidence, with the \( p \)-th order spectrum as the incident light \( (\theta' = \beta_p') \), becomes as

\[
v = \frac{v}{p} \sin \frac{npD}{\sqrt{1 - (p\alpha)^2}}
\]

because \( \sin \theta' = p\alpha \) in this case. This change, however, is of minor importance as compared to the change in phase, to be described below.

We have stated that the point \( B \) in Fig. 3 corresponds to the point where all the diffraction spectra in case of normal incidence are of the same phase, the convention of sign of \( A_s \) being admitted. Now this point shifts to \( B' \), halfway between \( BC \) in case of oblique incidence. Here \( C \) is the point where the central ray \( OC \) quits the ultrasonic beam. It means that the position of the phase-grating is shifted relative to the position of the sound wave in case of oblique incidence, as a result of the averaging out of the refractive index along the rays of light.

Now this point \( B' \) (for the \( p \)-th order light) is nearly in phase with the point \( B \) (for the \( 0 \)-order light), because \( B' \) is in phase with \( B \) in Fig. 3, and as

\[
OB - OB' = \frac{OC + OF}{2} - OB = L \left\{ \frac{L}{2} (\sec \beta_p' + \cos \beta_p') - 1 \right\} = L \left\{ \frac{L}{2} \left[ \frac{1}{1 - (p\alpha)^2} \right]^{1/2} - \frac{1}{1 - (p\alpha)^2} \right\}^{1/2}
\]

is a small quantity of higher order as compared to the path-difference produced after leaving the \( j \)-th sub-beam between the components \((p,s)\) and \((0,s)\):

\[
BG = \frac{L}{2} \tan \beta_p' \sin \beta_p' = \frac{L}{2} ps \alpha^2 \left[ 1 - (p\alpha)^2 \right]^{1/2}.
\]

So we have as the phase-difference between the \((p,s)\)-component and the \((0,s)\)-component

\[
\psi_{p,s} = \frac{2\pi}{\lambda} \left[ BG - (OB - OB') \right] = \frac{2\pi}{\lambda} \frac{psD}{\sqrt{1 - (p\alpha)^2}}
\]

The symmetry property of \( \psi_{p,s} \) follows immediately as

\[
\psi_{-p,s} = \psi_{p,s} = -\psi_{-p,s} = -\psi_{p,s}
\]

Here we employed geometrical terms in deriving these relations. The same result, however, is easily obtained also by computing the diffraction integral.
3. Scheme of the computation

The complex amplitude of the s-th order light emerging from the j-th sub-beam of sound is indicated as

$$A_s^{st} = A_s^j \exp i \phi_s^j, \quad (j=1,2,3,\ldots; \quad s=0,1,2,\ldots) \quad (11)$$

The obvious symmetry property

$$A_s^{st} = (-1)^s A_s^{-st} \quad (12)$$

is easily obtainable. Making use of (6), (8), (9), (10), and (12) we have the working formula in computing the complex amplitude $A_s^{st}$ from $A_s^{st}$:

$$A_s^{st} = A_s^{st}$$

$$A_s^{st} = A_s^{st} + A_s^{st}$$

$$A_s^{st} = A_s^{st} + A_s^{st}$$

$$A_s^{st} = A_s^{st} + A_s^{st}$$

$$A_s^{st} = A_s^{st} + A_s^{st}$$

$$A_s^{st} = A_s^{st} + A_s^{st}$$

We separate this into real and imaginary parts as

$$A_s^{st} = B_s^{st} + i C_s^{st} \quad (14)$$

and compute $B_s^{st}$ and $C_s^{st}$ by separate formulas. The light intensity becomes as

$$I_s^{st} = c_s (A_s^{st})^2 = c_s L_s^2 \quad (15)$$

where $c_s$ is the normalization constant.

The computation was performed by a digital computer OKITAG-5090 at the Institute of Industrial Science, University of Tokyo, for various values of $\theta = \text{const.}$ (0.2, 0.5, 1, 2, 3, 4, 5, 10, 20, and 100) and mainly in the range $v = 0 \sim 30$. Fig. 4 shows an example for $\theta = 10$ and is in complete agreement with the exact result of Extermann and Wannier up to $D = 1.0$, the upper limit of their calculation. The computation in this case is performed in 250 steps with intervals $D = 0.01$ ($v = 0.2$) up to $D = 2.5$ ($v = 50$). The value of $\chi$ is assumed to be $\chi = 0.0003$.

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In thermal equilibrium every collective mode of motion in a liquid experiences thermal fluctuations. These fluctuations will generally scatter light, and by analysis of the scattered light some properties of the fluctuations can be determined. We report here such studies of the thermal fluctuations of a liquid surface, the quanta of which have been referred to as ripplons. Assuming that classical hydrodynamics can be used in describing the thermal fluctuations, one finds that for wavelengths above a certain critical value, often of the order of $10^{-3}$ cm, the fluctuations can be described in terms of decaying underdamped oscillatory surface waves, ripples. Below the critical wavelength the oscillations are overdamped and decay exponentially without oscillations. When light is scattered by the underdamped oscillations, the spectrum of the scattered light is shifted by an amount equal to the frequency of the oscillations. The bandwidth of the scattered light determines the decay time of the oscillations. From measurements of the frequency shift and the bandwidth, the dispersion relation for the surface oscillations in this short-wavelength region can be determined. Furthermore, from the dispersion relation the value of the shear viscosity and the surface tension can be obtained. Scattering by overdamped fluctuations gives rise merely to a
Light Scattering from Thermal Surface Vibrations of Liquids

line broadening without a net frequency shift.

For underdamped fluctuations the scattering process can be regarded as a photon-ripplon collision in which energy and the component of momentum along the liquid surface are conserved. Energy conservation implies that the scattered light spectrum is a doublet of frequency \( \omega' \) and \( \omega' \), where \( \omega' \) and \( \omega' \) are the frequencies of the incident light and the ripplon. If this spectrum is observed in a direction \((\theta,\phi)\) below the surface, conservation of momentum implies that the wavelength \( \lambda \) of the observed ripplon is given by

\[
\lambda = (\lambda/n)(\sin^2\theta + \sin^2\theta_o - 2\sin\theta\sin\theta_o\cos\phi)^{-1/2},
\]

where \( n \) is the index of refraction, \( \lambda \) is the free-space light wavelength, and \( \theta_o \) is the polar angle of the light beam incident from below the surface. The surface vibrations are damped by viscosity, and the shape of the lines of the doublet is Lorentzian, with a half-intensity width \( \Delta \omega = 2/\tau \), where \( \tau \) can be considered the ripplon lifetime. By spectral analysis of the scattered light at different values of the angles \((\theta_o,\theta,\phi)\), we can determine the ripplon frequency \( \omega \) and lifetime \( \tau \) as functions of the wavelength \( \lambda \).

The experimental arrangement is as follows: Light from an argon ion laser, operating in the principal transverse mode at 4880 Å at a power of \( \sim 5 \text{ mW} \), is totally reflected from the liquid surface. The surface scattered light is collimated and recombined with a portion of the incident laser light at a beam splitter, and the combined beams are directed onto a photomultiplier. The resulting photocurrent, containing the difference frequencies between the two light beams, is filtered with an ultrasonic spectrum analyzer. To make the output of this analyzer proportional to the scattered-light spectrum (downshifted by an amount \( \omega' \)), a square-law detector (bolometer) is used at the i.f. output of the analyzer. To improve the signal-to-noise ratio, the scattered light is chopped before reaching the beam.
splitter, and the chopped output of the spectrum analyzer is fed to a synchronous detector and recorded.

Results obtained with methanol\textsuperscript{2} and with ether and glycol,\textsuperscript{3} the latter at comparatively low frequencies, have been reported. We now have studied fluctuations on other liquids, such as isopropanol, ethanol, and water, and also the fluctuations of interfaces between two liquids. For the pure liquids the values of surface tension and shear viscosity obtained from the measurements are in good agreement with statically measured values. In the wavelength region explored, between approximately 1.8 and 4 \times 10^{-3} \text{ cm}, the fluctuations are underdamped for the liquids considered, and a net frequency shift of the scattered light is observed.

On the other hand, the thermal fluctuations of the interfaces studied, for example, between methanol and hexane, were found to be overdamped in the wavelength region indicated above, and the effective surface tension of the interface was found to be as low as 0.08. An even lower surface tension was observed in scattering from a monolayer of oleic acid on water. Again, overdamped fluctuations were found, and a surface tension as low as 0.005 was found.

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References

Some Aspects of Laser Light Diffraction by an Ultrasonic Wave in Inhomogeneous Media

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Introduction

Light diffraction on an ultrasonic wave in inhomogeneous media liquid-vapour system: ethylene and CO₂ near the critical point, liquid-liquid system: aniline cyclohexane solution near the critical point of miscibility has been studied in recent years /1,2,3/ with usual light sources. The diffraction patterns from such inhomogeneous media exhibit fluctuations as a result of the large density or concentration fluctuations in the medium at the specific thermodynamical conditions near critical points, leading to widely diffuse principal diffraction fringes corresponding to a "diffraction grating" of constant \( \lambda \) equal to the ultrasonic wavelength sometimes splitting into a characteristic fine structure. A theoretical explanation was attempted /4,5/ invoking light diffraction on an ultrasonic wave scattered on the fluctuations.

It is of interest to follow these effects with classical source replaced by a laser. The present, preliminary observations already differ strongly from previous. This is due essentially to 1. high coherence of the laser beam, and 2. its large intensity.

Apparatus

Laser was He-Ne of power ca. 2 mW, \( \lambda = 6328 \) Å, supplied with DC voltage thus eliminating own fluctuations in brightness of the source. The measuring system is seen in Fig.1. The beam 2.5 mm in diameter from laser L traverses vessel A with inhomogeneous medium maintained at near critical thermodynamic conditions (thermostat T) where an ultrasonic wave (frequency 1 or 6 MHz) generated by quartz
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Q propagates perpendicularly to the beam. The light diffracted on the wave is focused with objective 0₁ and diffraction pictures are taken with camera C.

Fig.1. Optical system

Observations and discussion

In previous work with usual light the secondary source was a rectangular slit whereas here the beam is of circular cross-section as the source provides coherent light immediately. Consequently, the diffraction pattern is not a system of parallel fringes (images of the slit) but a system of circular dots representing the various orders of the spectrum (Fig.2a). With a laser beam, one gets multifold patterns and a characteristic system of circles about the spectrum proper (Fig.2b). Both pictures in Fig.2 were obtained for a homogeneous system far from the critical point at identical ultrasonic intensity of about 3 W/cm² (frequency 6 MHz). The multifold pattern of Fig.2b strongly resembles those obtained with usual light but with diffraction taking place on several ultrasonic waves /6/ or at high ultrasonic intensity (involving the second harmonic of the generated wave).

Fig.2 Ultrasonic light diffraction patterns for homogeneous medium hexane; a) usual light (monochromatic, green Hg line from a 50 W bulb) b) light from He-Ne laser

Presumably, the multifold diffraction of Fig.2b is due to non-linear effects occurring in the propagating ultrasonic wave and possibly to slight reflections thereof, to which usual light cannot react. Here, the high intensity and coherence of the laser beam both play a part.

The occurrence of inhomogeneities of the nature of density or concentration fluctuations in the medium (in vessel A) leading in the case of usual light to marked fluctuations of the patterns diffracted on the scattered ultrasonic wave now (with laser light) leads
to an immense differentiation of the patterns and their enrichment in details. Laser light is much more sensitive to local changes in the medium in the ultrasonic field than is usual light. Figs 3a-3d exemplify patterns obtained on fluctuations of concentration in a hexane-methanol mixture near the critical point ($t_{cr} = 41.4^\circ C$, $c_{cr} = 69\%$). In the process of fluctuation of the diffraction patterns as we approach the critical point, two stages can be distinguished, corresponding respectively to large-grain fluctuations (at a distance of 1-2$^\circ C$ from the critical point) and to critical light opalescence (within 0.1$^\circ C$ therefrom) /2/. Transition to the second stage is sudden as a result of the fluctuations breaking up. The presence near the critical point of large-grain in addition to fine-grain fluctuations was also established by Brown using a different method /7/. The diffraction pattern at opalescence becomes fully dispersed and can no longer be photographed. However, using a film camera, the successive stages of the transition can be followed.

Fig. 3 shows clearly the fine structure of diffraction patterns due to scattering on fluctuations of the Mandelshtam-Brillouin type.

Fluctuating patterns of diffraction on an ultrasonic wave similar to those of Fig. 3 are observed in CO$_2$ liquid-vapour system, although here perceptible differences occur with regard to the liquid-liquid system (critical solution) /8/.

Conclusions

The splitting of diffraction patterns into fine structure and their time-diffuence is so much more marked when using laser light than with usual light as to incite to a closer study of these effects.
Laser Light Diffraction by an Ultrasonic Wave in Inhomogeneous Media

in the hope of relating the results with thermodynamical and statistical theories of the critical point. Noteworthy in this respect is the work of Alpert et al. /9/ who studied He-Ne laser light scattering without ultrasonics in CO₂ in the immediate vicinity of the critical point in the opalescence region; the spectral composition of the scattered light was broadened by density fluctuations. In the case of the diffuseness of principal fringes of light diffraction patterns on ultrasonics observed by us, we also deal with light modulation on fluctuations in both the large-grain and fine-grain stages of fluctuations mentioned above.

Investigation of systems of the type exhibiting interaction of light scattering effects of the Mandelshtam-Brillouin type and diffraction of the Debye-Sears type is of much interest /6,10/. Interpretation of the patterns is as yet difficult. With the laser power available in our experiments, induced Mandelshtam-Brillouin scattering did not appear.

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On the Acoustic of Non-stationary Waves in Dissipated Media

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Introduction. Acoustic velocity is calculated for intensive waves in dissipated media in non-stationary conditions. When \( t \to \infty \), the wave equation becomes stationary.

Let us investigate the propagation of acoustic waves in dissipated media with an account of non-stationary phenomena. It is well known that both theoretical and practical difficulties are encountered in studying the non-stationary acoustic waves. This question becomes all the more complicated in studying the propagation of intensive acoustic waves in dissipated media. Inspite of the above difficulties, the author has made an attempt, at least to arrive an approximate solution to the problem by overcoming the very cumbersome calculations. By expanding in series and estimating the terms of gas dynamics equations as given in papers^1,2), it is possible to find an equation for the acoustic velocity

\[
\begin{align*}
\frac{\partial u}{\partial t} - \alpha \frac{\partial u}{\partial x} - \beta \frac{\partial u}{\partial t} = \lambda_1 \frac{\partial^2 u}{\partial x^2} + \lambda_2 \frac{\partial^2 u}{\partial t^2} + \lambda_3 \frac{\partial^3 u}{\partial x^2 \partial t} + \lambda_4 \left( \frac{\partial u}{\partial x} \right)^2
\end{align*}
\]  

(1)

The right hand side of (1) is the sum of terms of 3rd order
smallness and \( \mu \) is a parameter of first order smallness.
\[
Z = \mu x, \quad \tau = (t - \frac{X}{c_0})
\]
on putting \( u = \frac{k_0}{w} \frac{\partial w}{\partial \tau} \), the equation (1) can be approximately expressed as
\[
\frac{\partial w}{\partial \tau} + \frac{\partial^2 w}{\partial \tau^2} = D w \int \frac{\partial^2 w}{\partial \tau^2} \frac{d\tau}{w} \quad (2)
\]
Since the right hand side of (2) is small, let us apply iteration method to transform it. Boundary condition and variation range of the variables are
\[
\text{when } Z = 0, \quad W(\xi, \tau) = \xi, \quad 0 \leq \xi \leq +\infty, \quad -\infty \leq \tau \leq +\infty \quad (3)
\]
After the transformation, we obtain the non-homogeneous parabolic equation instead of (2). By applying Green's method to the obtained equation, we get an expression for \( W(\xi, \tau) \). Since \( U = \frac{k_0}{w} \frac{\partial w}{\partial \tau} \), we find an expression for acoustic velocity:
\[
U = \frac{k_0}{w} \left[ -\omega \int_k^\infty \xi \frac{e^{-k^2 \xi^2}}{\sinh k\omega \tau} - \omega e_k k^2 \xi \frac{e^{-k^2 \xi^2}}{\sinh k\omega \tau} + L_k (1 - e^{-k^2 \xi^2}) + \right] \]
\[
\frac{[I_0(m) + F_k k^2 \xi \frac{e^{-k^2 \xi^2}}{\sinh k\omega \tau} + e_k \xi \frac{e^{-k^2 \xi^2}}{\sinh k\omega \tau} + L_k (1 - e^{-k^2 \xi^2}) + \right] + 2 \omega M_k \left( e^{-k^2 \xi^2} - \frac{e^{-k^2 \xi^2}}{\sinh k\omega \tau} \right) + N_k e^{-k^2 \xi^2} \sinh k\omega \tau \quad (4)
\]
For the sake of simplicity, let us adopt the following notations for the operators:
\[ \begin{align*}
\mathcal{F}_k &= 2 \sum_{K \geq 1} (-)^K I_0^K(m) \\
\mathcal{E}_k &= \frac{D}{\omega} \sum_{K \geq 1} (-)^K I_0^K(m) K^3 \\
\mathcal{L}_k &= -\frac{D}{2\alpha} \sum_{K \geq 1} I_0^2(m) K^2 \\
\mathcal{M}_k &= -\frac{D}{4\kappa} \frac{1}{\omega} \sum_{K \geq 1} I_0^1(m) K \\
\mathcal{N}_{kn} &= -\frac{D}{\alpha} \frac{1}{I_0(m)} \sum_{n \geq 1} \sum_{K \geq 1} (-)^K I_0^2(m) I_0(m) \\
\end{align*} \] (5)

The expression (4) is the required wave equation for the acoustic velocity in non-stationary conditions.

When \( \omega \) increases without limit, the wave equation (4) becomes stationary at great distances.

\[ \begin{align*}
\mathcal{U} &= -\kappa \frac{2\omega}{\sqrt{\omega^2 + \omega^2}} \sum_{K \geq 1} \sum_{n \geq 1} \sum_{K \geq 1} (-)^K I_0^2(m) I_0(m) K \left( \frac{\kappa^2 n^2}{\kappa^2 + n^2} \right) \frac{1}{\omega} \sum_{K \geq 1} K^2 \\
&= -\frac{\omega}{\kappa} \frac{1}{\omega} \sum_{K \geq 1} I_0^2(m) K^2 + 2\sum_{n \geq 1} \sum_{K \geq 1} (-)^K I_0^2(m) I_0(m) \left( \frac{\kappa^2 n^2}{\kappa^2 + n^2} \right) \frac{1}{\omega} \sum_{K \geq 1} K^2 \\
&= \sum_{K \geq 1} I_0^2(m) K^2 + \sum_{n \geq 1} \sum_{K \geq 1} (-)^K I_0^2(m) I_0(m) \left( \frac{\kappa^2 n^2}{\kappa^2 + n^2} \right) \frac{1}{\omega} \sum_{K \geq 1} K^2 \\
&= \frac{\omega}{\kappa} \frac{1}{\omega} \sum_{K \geq 1} K^2 \\
\end{align*} \] (6)

CONCLUSIONS

1. An equation has been derived for the acoustic velocity in non-stationary conditions satisfying the given boundary conditions.

2. When \( \omega \to \infty \), a stationary equation is obtained for the waves with acoustic velocity at great distances from the source.

3. The non-periodic terms in the non-stationary acoustic velocity indicate that the positive and negative amplitudes of travelling wave are unsymmetric.
Notations used in the paper

$$\alpha_0 = \frac{(\psi+\frac{1}{2})}{2\mu \beta_3^2} \gamma + \frac{\epsilon}{\beta_3}, \quad \beta_1 = \frac{S_1}{\rho c}, \quad \beta_2 = \frac{S_2}{\rho c}, \quad \beta_3 = \frac{(\psi+1)\mu}{\rho c}, \quad \alpha = \frac{\delta}{\omega^2},$$

$$\delta = \frac{\left(\beta_1 + \beta_2\right)}{2\mu \rho \beta_3^2}, \quad \eta = \frac{2\mu \omega}{\rho \beta_3}, \quad \kappa_3 = \frac{2(\beta_1 + \beta_3)}{(\psi+1)\mu \rho \beta_3}, \quad m_0 = \frac{(\psi+1)}{2}\frac{\partial u_0}{\rho \beta_3^2}, \quad \mu = \frac{(\psi+1)}{2}\frac{\partial u_0}{\rho \beta_3^2},$$

$$\alpha_1^* = -\frac{(\psi+1)^2}{\eta}, \quad \alpha_2^* = -\frac{(3\psi+5)\beta}{2\mu \beta_3^2}, \quad \alpha_3^* = \frac{\beta}{2}\left(\frac{\gamma}{\beta_3} - \frac{\beta_3}{\beta_3^2}\right), \quad \alpha_4^* = \frac{1}{2}\frac{\partial u_0}{\rho \beta_3^2} - \frac{\beta_3}{\beta_3^2},$$

$$\beta^* = \frac{\beta^2}{\gamma} - \frac{\beta}{\gamma} \frac{\beta_3}{\beta_3^2}, \quad \gamma^* = \frac{(\psi+1)}{\gamma} \beta + \frac{\beta_3}{\beta_3^2} \frac{\beta}{\gamma},$$

$$\mathcal{F} = \frac{1}{8c_0^2} \left[ \frac{\psi}{\gamma} \beta_3^2 + \frac{\psi (\psi+1)}{\gamma} \frac{\beta_3}{\beta_3^2} \beta_3 \beta_3^2 + \frac{(\psi+1)(\psi+1)}{\gamma^2} \frac{\beta_3}{\beta_3^2} \beta_3^2 \right],$$

$$\mathcal{G} = \frac{1}{8c_0^2} \left[ \frac{\psi (\psi+1)}{\gamma} \beta_3^2 + \frac{\psi (\psi+1)(5\psi+3)}{\gamma} \beta_3 \beta_3^2 \beta_3^2 \right], \quad \beta = \frac{1}{2c_0} \left[ \frac{\beta_3}{\beta_3^2} + \frac{(\psi+1)\mu}{\rho \beta_3^2} \right]$$

$U_{\alpha}$ - amplitude of the piston.

$I_\nu(m_0)$ - Modified Bessel function.

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I. Introduction

The existing experimental information about ultrasonic cavitation in liquid helium consists of the following main features:

(i) The audible cavitation threshold maintains a fairly constant level between 1000 - 2000 dynes/cm² for both He II and He I for $T > 1.2\,^\circ\text{K}$, except in the neighborhood of $T_{\lambda}$, where the threshold rises to as high as 6,000 dynes/cm²\(^1\).

(ii) In He II, there is an order of magnitude difference between the visible and audible cavitation thresholds. Whereas no distinction is observed for He I\(^2\).

(iii) The audible threshold in He II is reduced, when the liquid is subject to rotation. The reduction commences when the rotating speed exceeds the value corresponding to the creation of one unit of quantized vortices. No such reduction is observed in He I\(^3\).

The questions implied in these experimental findings are many. In the following, we shall attempt to construct a theory which can at least qualitatively account for all these puzzling phenomena.
II. "Nuclei" and Cavitation in He I

The development of the theory is essentially based on the new interpretation of rotons in liquid helium. According to this new interpretation, rotons are considered to behave like tiny vortex rings. Among other properties, there is tension in the vortex core, given approximately by

$$T = \frac{\rho k^2}{4\pi}$$

where $\rho$ is the density of the liquid and $k$ is the circulation around the vortex core. For one quantum of circulation, $k = \frac{\hbar}{\pi m} = 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$, and $T = 10^{-8} \text{ dynes}$, which is of the same order of magnitude as the Van der Waals force in the liquid helium. It is to be stipulated that the Van der Waals force is somewhat larger than the vortex tension to prevent the spontaneous rupture of the liquid by the vortex tension. The spontaneous rupture does occur when the boiling point is reached, i.e., when majority of the rotons start to acquire enough quanta of circulation, say $n$ quanta, so that their tension in the vortex core exceeds the Van der Waals force.

Below the boiling point, the stable rotons are those with $(n-1)$ quanta or less. The tensile strength of the liquid then is controlled by these $(n-1)$-rotons, and their locality are where the nuclei of cavitation are generated.

The tension in $(n-1)$-rotons is smaller than the Van der Waals force, yet comparable. Their difference may be much smaller than the Van der Waals force. This residual force we take to represent essentially the tensile strength of the liquid. This also accounts for the low audible cavitation threshold of the liquid. The tension due to the imposed sound field may cause the formation of tiny bubbles by the rupture of liquid. These original bubbles, with radius $R_o$, will grow bigger with the aid of cosmic rays. Their subsequent collapse will give rise to noises identifiable with cavitation.

Analysis shows that the reasonable value of $R_o$ is about $10^{-5} \text{ cm}$. Then in He I, the energy deposited in the local region around the original bubble will enable the bubble to grow to a radius about $3 \times 10^{-4} \text{ cm}$ or more. At $R_c = 3 \times 10^{-4} \text{ cm}$, the audible threshold of 2, 000 dyne/cm$^2$ is sufficient to overcome the pressure due to the surface tension.

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and visible cavitation appears. Therefore, with the aid of the cosmic rays, there is no distinction between audible and visible cavitation thresholds in He I.

III. Cavitation in He II

The mechanisms for cavitation in He II are essentially the same as those for He I. There are, however, two main differences:

(i) The heat transfer in He II is controlled by the internal convection and is much more efficient than the thermal conduction in He I.

(ii) Not all the helium atoms partake in excitations to form rotons, so there is room for the creation of new excitations.

Therefore, although the audible cavitation threshold remains essentially the same as that of He I, the visible threshold will be different due to (i). For owing to the more efficient internal convection, the nuclei do not have time to grow to the size of $R_c$. They can grow to only $R'_c = 1.5 \times 10^{-3}$ cm, which corresponds to a visible threshold of about $4 \times 10^4$ dyne/cm$^2$. The efficiency of internal convection is controlled by the speed of second sound. The variation of visible threshold with temperature in He II corresponds also to the temperature variation of the speed of second sound.

The reduction of audible threshold in He II by rotation is explainable by (ii). Macroscopic quantized vortices or large rotons are produced by the rotation. Since the tension in the vortex ring is actually a slowly increasing function of its radius, therefore, if we have particularly large rotons present in the liquid, the negative pressure needed to break up these rotons will be less, and the audible threshold will be reduced. In He I, no unexcited helium atoms are left, hence no new quantized vortex rings may be created by rotation and we do not have the reduction of the cavitation threshold.

Now, the audible threshold, as a function of temperature, has a sharp peak at $T_\lambda$. This peak is closely related to the nature of $\lambda$-transition. The $\lambda$-point, besides being the lowest temperature at which all helium atoms are excited, also marks an order-disorder transition. The order refers to the arrangement and orientation of the rotons. The anomaly of the specific heat at $T_\lambda$ tells that a
Ultrasonic Cavitation in Liquid Helium

a substantial portion of the absorbed energy has to be spent on the destruction of the order before it can contribute to the kinetic motion. The process of breaking up the rotons, which inevitably involves the energy absorption, then would also require extra work if it is coupled with the destruction of order. It is interesting to note that the half width in temperature of the threshold peak is of the same order as that of the specific heat curve.

IV. Discussion

Further experimental research should be carried out in the following areas:

(i) Under condition that cosmic rays may be largely shielded off to firmly establish the role played by the cosmic rays;

(ii) At low enough temperature when the populations of excitations is dominated by the phonons rather than rotons.

The roton theory, if applicable to He I, should also be applicable to other liquids. The situation will undoubtedly be more complex, but the general picture as we have constructed for He I may still be valid. It is likely that the problems concerning the low tensile strength, and the nuclei of cavitation of ordinary liquids could be resolved by an analogous roton theory.

References

Hypothèse explicative de l'absence de sonoluminescence en cavitation de vapeur

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Introduction

Nous avons observé antérieurement un phénomène de relaxation entre deux modes de vibrations ultrasonores que nous avons reconnus être la cavitation de gaz (pseudo-cavitation) et la cavitation de vapeur (cavitation vraie) (1), (2), (3). En appliquant une puissance ultrasonore constante nous obtenons, dans certaines conditions, le passage spontané d'une cavitation à l'autre, chacune étant caractérisée par une intensité différente dans le liquide. Nous avons aussi établi que la sonoluminescence existe seulement en cavitation de gaz, (4), (5), (6).

Conditions expérimentales

Nous avons étudié la sonoluminescence dans l'eau et différentes solutions. Le volume irradié était choisi selon l'expérience entre 35 cm$^3$ et 150 cm$^3$. La fréquence utilisée a été le plus souvent 1 MHz, mais nous avons obtenu aussi des relaxations des cavitations dans la plage de 300 KHz à 3 MHz. La puissance acoustique globale (liquide dégazé) pouvait être variée entre 0 et 50 Watts. L'intensité de la luminescence a été mesurée dans le spectre visible par un photomultiplicateur d'électrons dont on enregistrerait la tension de sortie. L'irradiation se faisait dans une cuve parallélépipédique, la température étant déterminée à l'aide d'un thermocouple étalonné. L'intensité était mesurée à l'aide d'un 2ème thermocouple étalonné (à 2 soudures très rapprochées dont l'une était enrobée d'absorbant).
Résultats

1. Corrélation temporelle entre l'intensité de la sonoluminescence et la période des relaxations des cavitations.

Nous avons représenté à la figure I-a, la période de la relaxation des cavitations sous la forme d'un enregistrement de l'intensité I (densité de puissance) et de la température T, en un point du liquide, en fonction du temps, et à la figure I-b, l'enregistrement simultané de la sonoluminescence globale δ. Nous constatons que :
a). la luminescence a lieu seulement pendant la période τ₀ de la cavitation de gaz; l'intensité de cette luminescence δ n'est pas constante pendant cette période, elle passe par un maximum un peu avant la fin de la période (Fig. I-b); b). l'amplitude des variations brusques de I et de T (segments AB et CD), dépend du point où la mesure est faite. En déplaçant la soudure du thermocouple de température, on peut trouver plusieurs points où l'amplitude de ces variations devient presque nulle. La courbe T = f (t) devient une ligne brisée formée d'une succession alternée de segments de pente contraire; les segments AB et CD sont dus au fait que dans les deux états les mouvements convectifs au sein du liquide sont différents; il y a un ajustement de la température à chaque état.

Au contraire, pour I, on trouve toujours cette brusque augmentation au moment du passage à la vraie cavitation. En effet, dans ce nouvel état la résistance de rayonnement du milieu augmente. Nous constatons encore que : a). dans la période de pseudo-cavitation (BC), I et T augmentent avec le temps; b). dans les périodes de cavitation vraie (DA), I et T diminuent avec le temps.

2. Relation entre les intensités mesurées et les deux cavitations.

La figure II montre qu'à la puissance H on peut mesurer dans le liquide deux intensités différentes : CH en pseudo-cavitation, DH en vraie cavitation. Or, le passage d'une cavité stable à une cavité
Hypothèse explicative de l'absence de sonoluminescence...

transitoire a lieu, en absence de pertes, lorsque le Δp produit dans le liquide par l'onde ultrasonore plane et sinusoidale devient environ égal à la pression extérieure (\(\sim 1\) bar) (7) (8). A la puissance \(\Pi_1\), l'intensité \(I_1\) conduit à \(\Delta p_1 = 1,85\) bar (9). La différence entre cette valeur et la valeur théorique de 1 bar correspondrait grosso modo à la dissipation d'énergie des bulles pulsantes dans le champ ultrasonore. En partant du travail de SPITZER (10), on peut calculer l'ordre de grandeur de la dissipation. Il calcule le décroîtment logarithmique \(\Lambda = \Lambda_t + \Lambda_v + \Lambda_\alpha\) de l'amplitude d'oscillation d'une bulle de rayon \(r = 13\mu\) (où \(\Lambda_t, \Lambda_v\) et \(\Lambda_\alpha\) sont respectivement les décroîtments thermodynamique, viscosité et acoustique). A la fréquence de 1 MHz, \(\Lambda \sim 0,47\), et pour ce décroîtment le rapport entre Δp mesuré (Δp_m) et Δp utilisé pour le mouvement de la bulle (Δp_u) est : \(\Delta p_m / \Delta p_u = e^{0,47\Lambda \sim 1,7}\), d'où : \(\Delta p_u = \Delta p_m / 1,7\) = 1,85/1,7 \(\sim 1\) bar. Par cette voie nous retrouvons la valeur théorique calculée par NOLTINGK et NEPPIRAS. Notons que la valeur de \(\Lambda\) calculée pour une bulle n'est probablement pas tout à fait la même pour la population de bulles présentes dans le liquide, mais c'est un ordre de grandeur. Ainsi, à des puissances inférieures à \(\Pi_1\), \(\Delta p_u \ll 1\) bar. A la puissance \(Q\) (seuil de pseudo-cavitation), \(\Delta p_u \sim 0,3\) bar. Il apparaît donc qu'en pseudo-cavitation nous sommes en présence de cavités stables (Δp_u \(\ll 1\) bar).

A une puissance supérieure à \(\Pi_1\), nous sommes en vraie cavitation. Si nous supposons que dans cette cavitation les pertes thermodynamiques dans le gaz ont disparu, le rapport de réduction entre \(\Delta p_m\) et \(\Delta p_u\) doit être inférieur à 1,7; alors \(\Delta p_u \gg 1\) bar (\(\Delta p_m = 2,53\) bars pour \(I_2\) à la puissance \(\Pi_1\)); nous sommes en présence de cavités transitoires et cela est encore plus vrai pour des puissances supérieures à \(\Pi_1\).
Hypothèse explicative de l'absence de sonoluminescence...

3. Explication de l'extinction de la sonoluminescence en cavitation de vapeur.

La sonoluminescence existe en pseudo-cavitation (cavités stables), mais est nulle en vraie cavitation (cavités transitoires) (Fig.1-b). Il faut donc modifier le modèle qui attribue la sonoluminescence à l'échauffement adiabatique du gaz, produit par l'implosion des cavités transitoires de vapeur. Il faut supposer que ces cavités se referment sans produire de transformations thermodynamiques importantes, et admettre que, puisque ces cavités contiennent principalement de la vapeur à la fin de leur période de grossissement, cette vapeur se recondensera pendant la période de l'implosion en entraînant dans le liquide les molécules gazeuses présentes. Ainsi, dans un faible volume autour du point où la cavité se referme le liquide sera sursaturé en gaz, car à la fin de l'implosion l'augmentation de la pression en ce point produira une augmentation de la solubilité. Lors de la décompression cette sursaturation locale produira un noyau de gaz qui servira à l'amorçage d'une nouvelle cavité transitoire de vapeur.

Conclusion

Nous avons constaté simultanément dans la vraie cavitation la présence de cavités transitoires de vapeur et l'extinction de la sonoluminescence, ce qui nous amène à supposer que chaque cycle ultrasonore doit s'effectuer sans transformations thermodynamiques importantes. Nous proposons l'hypothèse qu'à la compression les molécules de gaz, tout comme celles de vapeur, sont entraînées dans le liquide. L'existence de la luminescence en pseudo-cavitation, régime de cavités stables, exclut une explication par une hypothèse thermique; il s'agit donc probablement d'un phénomène électrique au niveau de la surface des bulles.

BIBLIOGRAPHIE

Sonoluminescence from Water containing Dissolved Gases.

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Introduction

Srinivasan and Holroyd (1), Parke and Taylor (2), Gunther et al (3), and Prudhomme and Guilmart (4) measured the relative intensities of the sonoluminescence from eight different gases dissolved in water.

The experiment here was designed to provide a comprehensive study of seventeen different gases dissolved in water, including all the rare gases and the first four saturated hydrocarbons, using a photomultiplier tube sensitive from 1650 Å to 6500 Å.

Experimental Arrangement

Fig. 1 shows the essentials of the apparatus. A 20KHz Mullard Ultrasonic Transducer Type L533 joined to a titanium double quarter-wave velocity transformer cavitated degassed water in a pyrex beaker at an acoustic power of 10 watts corresponding to a sound pressure amplitude of 6.4 atmospheres in water. Gas could be bubbled through the water to first produce a saturated solution. The sonoluminescence was measured by a 13 stage EMI photomultiplier tube 6255B. Fig. 2 is a block diagram of the measuring equipment.

Results

For each gas, the result given is the average of between five and ten determinations, these usually agreeing to about 4%. Fig. 3 is a table of results of
seventeen different gases dissolved in degassed water, compared with the results for the rare gases obtained by Prudhomme and Guilmart (4) using a photocell operating in the range 1900 Å to 2800 Å; and obtained by Muller (5) in which the light in the range 4000 Å to 6000 Å was measured from glass bulbs of gas imploded in water. In the last group of gases, the very low values for carbon dioxide and hydrogen are of interest since Griffing and Sette (6) found that the sonoluminescence was non-existent for these gases.

If the sonoluminescence is basically due to an adiabatic compression during the rapid collapse of the cavitation bubbles, then any loss of energy of the gas molecules due to thermal conduction will modify this simple theory and cause lower final temperatures. Thus the luminous intensity will be dependent on the thermal
### Table of Results

<table>
<thead>
<tr>
<th>Gas</th>
<th>Luminous Intensity at Photocathode. Young</th>
<th>Sonoluminescence Prudhomme &amp; Guilmard Relative results</th>
<th>Total Radiation Energy. Muller Ws.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1690 Å - 6500 Å</td>
<td>1900 Å - 2800 Å</td>
<td>4000 Å - 6000 Å</td>
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<td>Air</td>
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<td>1</td>
<td>0.002</td>
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<tr>
<td>Nitrogen</td>
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<td>18</td>
<td>0.014</td>
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<tr>
<td>Oxygen</td>
<td>2.40</td>
<td>54</td>
<td>1.3</td>
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<tr>
<td>Helium</td>
<td>1.16</td>
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<td>3.20</td>
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<td>Nitrous Oxide</td>
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<td>Freon</td>
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<tr>
<td>Hydrogen</td>
<td>0.86</td>
<td></td>
<td></td>
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</tbody>
</table>

Fig. 3. Table of Results

Conductivity of the gas if there is time for heat conduction to occur. Figs. 4 and 5 are graphs of the luminous intensities against thermal conductivity for the rare gases and for the first four saturated hydrocarbons. Clear inverse relations are seen.

There is some doubt as to the effect of the solubility of the gas on the sonoluminescence. Hickling (7) concludes that, provided there is sufficient gas present, it is not certain that the luminous intensity should be strongly dependent on the
Sonoluminescence from Water containing Dissolved Gases

The results afford evidence for the hot spot theory of sonoluminescence though this may be modified in certain cases by excitation of the involved substances as pointed out by Muller (5).

References.
Quantitative distribution
cavitation nuclei.

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According to the estimation [1] the tensile strength of the absolutely pure water, caused by the temperature fluctuations, is about 2000 atm. However the tensile strength of the real water determined experimentally turns out much smaller. For example the largest tensile strength of the specially prepared water makes up only about 300 atm [2-4].

The discrepancy between the experimental tensile strength and the theoretical one in a real water may be explained by the presence of the different admixtures strongly reducing tensile strength of water.

It is known from the kinetic theory of liquid, that dissoluble or well wetted admixtures cannot appreciably reduce the tensile strength of the liquid because their contact angle is about zero.

Even badly wetted surfaces, the contact angles of which are about 50-60°, after staying in the water for some days have the contact angles near by 0° [5]. It takes place due to the progressive dissolution of the air adsorbed by the surface.

However often there are different kinds of pits and microcracks on the surfaces of the real solid particles. If the liquid does not wet the crack then the interface between the liquid and the gas trapped in the crack will be convex relative to the apex of the pit.
Quantitative distribution cavitation nuclei

In this case the liquid will not fill completely a crack at any finite pressure. Therefore the origin of the bubble owing to the tension of a liquid always begins from the vapour-gas phase having place in a such crack or pit.

The gas bubbles constantly present in a water have the greatest influence on the tensile strength of a water. The causes of the origin of the gas bubbles are evident (the trapping of the gas volumes in a water and their crushing with moving of water) but their existence for a long time at the first sight is doubtful. Nevertheless the numerous experiments 6-8 and others showed that the tensile strength of a liquid, preliminary exposed to the degassing or superposition of the raised hydrostatic pressure, had increased. It means that there are stable bubbles in the liquid, the number and the radius of which decrease in comparison with those in the normal conditions.

Without examining the causes of the stable existence of the gas bubbles, mechanism of which is not clear till now, we can state with confidence that from all different admixtures being in liquid its tensile strength depends essentially on the vapour gas bubbles constantly present in the small cracks of the suspended solid particles. When a bubble moves out of the pit or crack, preserving the shape of a hemisphere it may be represented as a vapour-gas nucleus with radius R, being equal to radius of the crack mouth.

If the stretching pressure does not reach the critical value $P_\infty$, the bubble is in stable state. At subsequent increase of the pressure $P_\infty$ bubble loses its stability and begins to grow sharply—and then collapses. From the differential equations describing the behaviour of the cavitation bubble as a function of time [9], follows that its radius depends to some extent on the kinetic energy of the added mass of a liquid.

Figure I shows value $P_\infty$ corresponding to the threshold of the cavitation onset in a water for nucleus with radius $R_o$. This curve
Quantitative distribution cavitation nuclei

![Graph showing the relationship between cavity radius and cavity number density](image)

was obtained on the base of the numerical solution of the Nolti-ngk-Neppiras equations of a gas bubble in the sound field with frequency of 10 kHz. Diffusion of a gas inward the bubble is neglected (it may be done for one or some cycle of the oscillations). The solid part of the curve corresponds to the cavities with radii up to $10^{-7}$cm. At the first because such small dimensions of the bubbles it is difficult to make theoretical consideration of the bubble behaviour; the application of the macroscopic thermodynamic parameter for the description of the system with some thousands of molecules may seems to be insufficiently based. However the successful development of the bubble camera theory shows that a such description may be used even for smaller system [10]. Thus it is not strange, that the calculation, made for the cavities with radius more than $10^{-7}$cm - right up to inter-molecular size (the dotted part of the curve), results in approximately the limit value of the tensile strength, obtained from the kinetic liquid theory.

Since there are the bubbles with the different dimensions in a liquid its tensile strength is a statistic conception, connected with the probability of hitting of the nucleus of some size into the sound field with the known intensity. Such a view about the tensile strength had been first introduced by Massino, Sette and Wanderling [11]. The multiple experiments, carried out by the authors of this report, permitted to find the number of the nuclei in the distilled water with the unit volume which were able to cause the cavitation in some small interval of the sound pressure.

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By using the dependence between $R_n$ and $P_n$, shown on the figure I, we can obtain the distribution function of the gas nuclei over the sizes.

Figure 2 shows the distribution of the vapour-gas cavitation nuclei over the sizes in the distilled water standing undisturbed for several hours. The points and crosses denote the counted again experimental data obtained in the paper [11]; the circles - the experimental results of our measurements [12]. The average curve, drawn according to these experimental data asymptotically does to the nuclei, the radii of which correspond to the inter-molecular distance (the dashed part of the curve). If the solid curve gives the concentration of the nuclei in the form of the bubbles with radii up to $10^{-7}$cm, its dashed part concerns nuclei, which represent the vapour ones due to the thermal fluctuations or produced by the $\delta$ - electrons by passing of the high energy particles.

**Literature**

A Connection between Nonlinear Elasticity and Ultrasonic Attenuation

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A more general formulation of the ideas of Akhieser\(^1\) and Mason\(^2,3\) gives a general theory of the contribution of thermal vibrations to mechanical energy dissipation in crystals. The two basic ingredients of the theory are the quasiharmonic approximation of lattice dynamics and an assumed equation of evolution that describes how the thermal modes return to equilibrium after they are perturbed.

In the quasiharmonic approximation the system energy levels are

\[
E_i(V) = \phi_0(V) + \sum_q \left( n_q^i + \frac{1}{2} \right) \hbar \nu_q(V), \quad n_q^i = 0, 1, 2, \ldots \quad (1)
\]

Here \(V\) stands for all six independent components of macroscopic strain. The vibrational part of \(E_i\) is a sum of harmonic oscillator energies. There is one term in the sum for each normal mode of vibration, \(q\). The set of occupation numbers \(n_q^i\) describes the microscopic state of a system.

To describe macroscopic states, we consider an ensemble of systems, and use the ensemble averages as macroscopic variables. Let \(g_1\) be the fraction of systems with the set \(n_q^i\). Then in general

\[
\sum_1 E_1 = 1, \quad U = \sum_1 E_1 g_1, \quad S = - k \sum_1 g_1 \ln g_1. \quad (2)
\]

Here \(U\) is the average energy per system, \(S\) the entropy, and \(k\) the Boltzmann constant. From (1) and (2),
\[ U = U_0 + \sum_q n_q h v_q, \quad U_0 = \Phi_0 + \sum_q \frac{1}{2} h v_q, \quad n_q = \sum_i \frac{1}{q} n_1^i. \]  \hspace{1cm} (3)

These equations hold for any distribution \( g_1 \), not just the equilibrium one. The equilibrium distribution is defined as the one that maximizes the entropy for a given energy. The results of this maximization problem are the standard thermodynamic formulas for a system of harmonic oscillators. For example, the equilibrium occupation number is \( \bar{n}_q = (e^{h v_q / kT} - 1)^{-1} \). The \( \bar{n}_q^i \) are integers but the ensemble averages \( \bar{n}_q \) are not. The numbers \( \bar{n}_q \) will be treated as continuous variables.

The other basic assumption of the theory is that the ensemble-averaged occupation numbers \( \bar{n}_q \) satisfy the differential equations
\[ \dot{\bar{n}}_q = \sum_r P_{qr}(n_r - \bar{n}_r), \quad \text{or} \quad \dot{n} = P(n - \bar{n}). \]  \hspace{1cm} (4)

Here \( \bar{n}_r \) is the equilibrium value of \( n_r \) that corresponds to the instantaneous strain and energy, and the dot denotes the time derivative. The coefficients \( P_{qr} \) are allowed to depend on the strain and energy. In the second form of (4), \( n \) and \( \bar{n} \) are single-column matrices and \( P \) is the square matrix of components \( P_{qr} \).

The energy required to produce adiabatically a homogeneous time-dependent deformation can be calculated from (3) and (4). The initial conditions are set by starting at equilibrium. All six components of a homogeneous adiabatic strain \( V_0 \) are prescribed by
\[ V_0(t) = \varepsilon_0 f_0(t), \quad \alpha = 1, 2, \ldots, 6, \]
\[ f_0(t) = 0 \quad \text{on} \quad t < 0, \quad |\varepsilon_0| << 1, \quad \max f_0(t) = 1. \]  \hspace{1cm} (5)

The energy can now be calculated as a power series in the small parameters \( \varepsilon_0 \), with coefficients that are functions of the time. The instantaneous stresses \( T_0(t) \) can be calculated from the definition
\[ dU(t) = v_0 \sum T_0(t) dV_0(t). \]  \hspace{1cm} (6)

Here \( v_0 \) is the initial (reference) volume of the system. In a finite strain theory, if the \( V_0 \) are the classical "Lagrangian" strain components, then the \( T_0 \) are called the components of the second Piola-Kirchhoff stress tensor. They reduce to the ordinary stress com-
ponents at the reference configuration or in infinitesimal strain theory. Since the six strain components are prescribed independently, \( T_\alpha(t) \) can be identified as the coefficient of \( \dot{V}_q(t) \) in an expression for \( \dot{U}/v_\circ \). The result for \( T_\alpha' \), up through terms linear in \( \varepsilon_\alpha \), is
\[
T_\alpha(t) = \bar{e}_\alpha + \sum \int_0^\infty g_{\alpha\beta}(t-p)\dot{V}_\beta(p)dp,
\]
\[
g_{\alpha\beta}(s) = 0, \quad s < 0 \\
= \left[ c_{\alpha\beta}^S - \frac{\hbar}{v_\circ} \frac{\partial v_\circ}{\partial v_\alpha} e^{-P_s(\partial T/\partial V_\beta)^S} \right]_0^s, \quad s > 0. \tag{7}
\]
Here \( \bar{e}_\alpha \) represents the \( \varepsilon_\alpha \)-independent initial stress, \( c_{\alpha\beta}^S \) the adiabatic elastic constants, \( v \) the row-vector of components \( v_q \), \( \hbar \) Planck's constant, and the index 0 indicates evaluation at the initial state.

The present theory is limited by the assumptions of the quasi-harmonic approximation and homogeneous straining, but is general enough to include any data concerning the distribution of normal mode frequencies and their dependence on the strain (nonlinear elasticity), as well as a large variety of assumptions concerning the kinetics of the return to equilibrium. It is interesting to note that (7) has the form of the relaxation integral law of macroscopic linear viscoelasticity, but the present theory also provides an expression for the relaxation function \( g_{\alpha\beta} \) in terms of microscopic parameters. From
\[
\Pi_q = \left( e^{\frac{\hbar v_q}{kT}} - 1 \right)^{-1}, \quad \left( \frac{\partial \Pi_q}{\partial V_\beta} \right)_T = -\frac{T}{v_q} \frac{\partial v_\beta}{\partial T} \left( \frac{\partial T}{\partial V_\gamma} \right)_V
\]
From Ref. 6,
\[
\left( \frac{\partial \Pi}{\partial V_\gamma} \right)_S = -\frac{T}{v_\circ} \left( \sum c_{\alpha\beta}^S \right) \]
where \( C_\alpha \) and \( c_{\alpha\beta}^S \) denote the specific heat per unit mass and expansion coefficient \( \partial V_\beta/\partial T \) at constant thermodynamic tensions, \( c_{\alpha\beta}^S \) the adiabatic elastic constants, and \( \rho_0 \) the density at zero strain. Then, writing \( \left( \frac{\partial \Pi}{\partial T} \right)_V = C_q/v_q \left( \frac{1}{v_q} \frac{\partial v_\gamma}{\partial v_\alpha} + \frac{1}{v_\circ} \sum c_{\alpha\beta}^S \right) \], then
\[
\left( \frac{\partial \Pi_q}{\partial V_\gamma} \right)_S = -\frac{Tc_q}{v_q} \left( \frac{1}{v_q} \frac{\partial v_\gamma}{\partial v_\alpha} + \frac{1}{v_\circ} \sum c_{\alpha\beta}^S \right).
\]

The strain derivatives of the normal mode frequencies thus enter quadratically into (7). Brugger\(^7\) has related their long wavelength limits to second- and third-order elastic constants.
A Connection between Nonlinear Elasticity and Ultrasonic Attenuation

If (7), derived for homogeneous strain, is assumed to apply locally in a wave, the attenuation can be calculated. The approach indicated by Prohofske\textsuperscript{8} corresponds to a special case in which the matrix \( P \) is diagonal. Mason's theory of ultrasonic attenuation by phonon viscosity emerges as a special case in which (1) \( P = I/\tau \), \( I \) being the unit matrix and \( \tau \) a scalar, (2) \( \tau \) is related to the lattice thermal conductivity, (3) additional assumptions resembling those of the Debye theory of specific heats are used to evaluate the needed derivatives of \( \nu \) and \( \bar{n} \) in terms of experimentally determined second- and third-order elastic constants. In the approximation of small damping, the attenuation constant resulting from (7) takes the form

\[
\alpha(\omega) = \frac{\omega}{2c_0} \sum q \frac{\omega \tau^2}{q^2} \frac{K^2}{1 + \omega^2 \tau^2}.
\]

(9)

This is a sum of terms of the relaxation type. Here \( c_0 \) is the low-frequency wave speed, the \( \tau_q \) are the reciprocals of the eigenvalues of the matrix \( P \), and the numbers \( K_q^2 \) are "known" factors involving sums of products of the strain derivatives occurring in (7).

References
On the Variation of Ultrasonic Cavitation Threshold according to Radiation Surface Materials

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Introduction

Ultrasonic cavitation has long been investigated and a number of research results are available. It is not easy, however, to obtain necessary technological values from those data in such a case as generation of intense ultrasonic waves in water by various transducers. One of the reasons for this is that it is difficult to describe ultrasonic cavitation by quantitative values useful in technology. The present authors previously proposed\(^1\)
\(^2\)
\(^3\) a method of approach in which the cavitation is evaluated quantitatively by the acoustic radiation resistance of an ultrasonic transducer generating ultrasonic cavitation. The proposal is based on the development of some methods by which the resistance is easily measured through electrical values only which are observable at the electrical terminal of the transducer. The cavitation threshold is distinctively determined by the point at which the radiation resistance begins to make a sharp fall. Moreover, the measurement of the radiation resistance is a useful method for obtaining sound pressure and acoustic power on the radiation surface quantitatively even in the case of intense ultrasonic radiation, and the radiation resistance characteristics also have important relationship with the discussion on the ultimate output power available from ultrasonic vibrators. The present authors et al. previously observed the variation of acoustic radiation resistance in relation to the variation of vibrational velocity of the transducer, the parameters for the observation being (1) the kinds of acoustic medium, (2) the air concentration in liquid and (3) ultrasonic frequency, and in the case of pulsed radiation, (4) the pulse length, (5) the repetition period, etc., being the additional parameter. Interesting results have been reported.\(^4\)

The authors have also been observing the effects of physical states of radiation surfaces (such as their roughness, their materials, etc.) on the generation of ultrasonic cavitation in water, and have recently found some interesting results which
Ultrasonic Cavitation Threshold according to Radiation Surface Materials

will be reported in this paper.

Relationship between surface roughness and cavitation

Specimens of different roughness were prepared (20 x 38 x 2 mm³ in size) and each was bonded on the radiation surface of a ferrite magnetostriction vibrator. The materials of the observed specimen were ferrite, stainless steel and bakelite. The surface of each specimen was ground by #400 and #80 mesh carborundum to obtain six different specimens. Fig. 1 shows the measured results, the ordinate being the radiation resistance value $r_a$ normalized by the value $(r_a)_0$ at small signal and the abscissa being the vibrational velocity $\nu$ of the specimen surface.

As seen in the figure, in the case of ferrite surface, the characteristics of the resistance fall very little differ from each other between the rough surface (ground by #80 mesh carborundum) and the smooth one (ground by #400 mesh). But, in the case of bakelite and stainless steel, a distinct difference is seen as smooth surfaces (#400 mesh) have higher cavitation threshold than rough surfaces (#80 mesh). The threshold value itself, however, is different between the materials though the roughness of the surfaces is equal.

Difference in cavitation threshold between radiation surface materials

As the observation in this case needed larger vibrational velocities, a solid horn was bonded on a ferrite magnetostriction vibrator of vibrometer type so that about two times larger amplitude was obtained. On a half-wave rod resonator, the specimen was bonded on its end surface and the rod was screwed at the tip of the solid horn as shown in Fig. 2. In this way, the specimens were easily exchanged. The materials tested

---

Fig. 1 A typical relation between the roughness of sound radiation surface and the radiation resistance under ultrasonic cavitation. Frequency: 28KHz, acoustic medium: water with air concentration 70% of the saturation value.

Fig. 2 Vibrometer type ferrite magnetostriction vibrator with solid horn and half-wave rod resonator with specimen.
are mainly teflon, polyethylene, urea, bakelite and glass. Merely for a reference, ferrite, barium titanate ceramic and stainless steel were also observed. Fig. 3 (a) and (b) show the typical data. The surface of each specimen was made chemically clean by an ultrasonic cleaner.

In Table I are summarized the values of cavitation threshold in this observation. Physical values, which characterize the surface state of the specimens in water, could be their roughness and wettabiity --- a certain measure relating to the energy of adhesion to water. The contact angle can represent this sort of wettabiity. In the table, the measured roughness and the contact angle are also shown. Throughout this observation, the roughness was nearly equal among all the specimens; and therefore, if the threshold values are compared with the contact angle values, it is found that the smaller the contact angle is, that is, the more wettable the surface is, the larger the threshold yields, and it is also found that this nature does not change with the air concentration of the water. But, stainless steel and ferrite are exceptions.

Consideration

First, with regard to Fig. 1 which relates with roughness, it is clear that the effect of roughness on cavitation threshold does not appear when the radiation surface is ferrite but does in the case of bakelite and stainless steel. This distinct difference may be explained as follows: A number of pits, though microscopically small, exists on the surface of sintered material such as ferrite, and the pits play a rôle to supply and to preserve cavitation nuclei and/or to multiply their number. A similar tendency (ref. Table I) was also observed in barium titanate.
Ultrasonic Cavitation Threshold according to Radiation Surface Materials

<table>
<thead>
<tr>
<th>Material of specimen</th>
<th>Roughness C.L.A. (μ)</th>
<th>Contact angle (°)</th>
<th>Tensile strength (kg/mm²)</th>
<th>Cavitation threshold* (air concentration)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>0.1 - 0.15</td>
<td>56</td>
<td>55% - 60</td>
<td>28%</td>
</tr>
<tr>
<td>Glass</td>
<td>&lt; 0.02</td>
<td>33</td>
<td>--</td>
<td>30%</td>
</tr>
<tr>
<td>Bakelite</td>
<td>0.02 - 0.05</td>
<td>48</td>
<td>4.5% - 6.0</td>
<td>30%</td>
</tr>
<tr>
<td>Urea</td>
<td>0.05 - 0.08</td>
<td>53</td>
<td>1.4% - 5.6</td>
<td>28%</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.08 - 0.1</td>
<td>84</td>
<td>1.2% - 3.8</td>
<td>25%</td>
</tr>
<tr>
<td>Ferrite</td>
<td>0.3 - 0.35</td>
<td>63.5</td>
<td>--</td>
<td>10%</td>
</tr>
<tr>
<td>Barium titanate</td>
<td>0.15 - 0.5</td>
<td>--</td>
<td>--</td>
<td>8%</td>
</tr>
<tr>
<td>Teflon</td>
<td>0.4 - 0.45</td>
<td>91</td>
<td>1.5% - 4.0</td>
<td>8%</td>
</tr>
</tbody>
</table>

* The values are shown by the vibrational velocity \( v \) in cm/sec. The ultrasonic frequency is 29 KHz.

...ceramic which is always produced by sintering process as ferrite is.

Second, with regard to Figs. 2 and 3 and Table 1 which relate with wettability, it is evident, except stainless steel and ferrite, that the cavitation threshold is higher when the surface material is more wettable. This nature may be explained as follows: A surface more wettable adheres to water more strongly, and makes the generation of cavitation nuclei difficult. Even though such small bubbles which may act as the nuclei could be generated, there might exist such mechanism that they leave the surface easily and are dissolved in the water immediately. Thus, the preservation of the nuclei are harder on the surface which is more wettable. Before reaching a conclusion in this phenomenon, however, it is necessary to make deep consideration theoretically in such a way as to give a model by which the mechanism stated above or other alternatives are represented. The energy of adhesion of stainless steel to water has been said not to be represented only by the contact angle. In the consideration, therefore, this material should be eliminated from Table 1.

The tensile strength of the materials are also shown in the table. Viewing from this point only, it is found that the larger the strength is, the higher the cavitation threshold yields. The value of the strength, however, is parallel in their order of magnitude with the wettability which is physically independent of the former. These facts make the consideration complicated and it is necessary in future to find a method of separation in the observation.

References

Spectral characteristics of cavitation noise

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One of the characteristic features of cavitation is the noise caused by the cavitation bubbles in some region of a liquid. In the case of the stationary cavitation region, formed in the field of the acoustic wave (acoustic cavitation) or in the field of the hydrodynamic pulsations (hydrodynamic cavitation), the noise pressure $F_N(t)$, caused by the radiation of $N$ cavities, is represented in the form $[1,2]$

$$F_N(t) = \sum_{k=0}^{N} \sum_{\epsilon=-\infty}^{\infty} \Psi(t-\epsilon 2\pi / \Phi(t), \epsilon_k, \nu_e),$$

(1)

where $\Psi(t, \epsilon_k, \nu_e)$ - function, characterizing the shape of the elementary signal radiated by the $K$-th cavity at the $\epsilon$-th period of the exciting wave; $\Phi(t)$ - the phase of this wave; $\epsilon_k$ and $\nu_e$ - random variables determining fluctuations of the parameters of the elementary signals according to their number $K$ and the time for the $K$-th cavity. We will assume, that the number $N$ of the elementary signals occurring on some interval of the time $T$, obeys a Poisson law of distribution. In case of the acoustic cavitation the correctness of this law for the number of cavities occurring in the cavitation region was tested experimentally $[1]$. Besides that in the process of the acoustic cavitation as well as hydrodynamic one in the region where the exciting pressure exists we can always choose rather big cavitation volumes in
Spectral characteristics of cavitation noise

which characteristics of these pressures are homogeneous and consequently statistical characteristics of cavitation noise are practically constant. In each region the cavitation bubbles on collapse break up into small parts and dissolve in liquid but with expanding they coagulate with each other and because of the diffusion they grow. So with the time passing the behaviour of some \(K\)-th cavity obeys the same statistic regularities as the behaviour of the group of the cavities for the region. It means that signals \(\varphi(t, \xi, \hat{y})\) form ergodic ensemble that permits to reduce to the problem of consideration of the signal characteristics \(\varphi(t, \hat{y})\) for any cavity.

Under the assumptions formulated above the model of the cavitation noise (I) permits to determine different statistic characteristics of noise and namely his power spectrum.

\[
G_F(\omega) = G_{F1}(\omega) + G_{F2}(\omega),
\]

where \(G_{F1}(\omega)\) and \(G_{F2}(\omega)\) - two components of spectrum with first one beign determined by characteristics of the exciting wave and the shape of elementary signals but second - by random changes of parameters of these signals.

In the case of acoustic cavitation excited in the field of the harmonic wave at the frequency \(\omega_0 = \frac{2\pi}{T_0}\), we have

\[
G_{F1}^a(\omega) = \frac{2\langle N \rangle}{T_0^2} \left| g(\omega, \hat{y}) \right|^2 \sum_{n=-\infty}^{\infty} \delta(\omega - n \frac{2\pi}{T_0}),
\]

\[
G_{F2}^a(\omega) = \frac{\langle N \rangle}{T_0} \left[ \left| g(\omega, \hat{y}) \right|^2 - \left| \overline{g(\omega, \hat{y})} \right|^2 \right]^2,
\]

where \(\langle N \rangle\) - the mean number of the cavities in the region under consideration, \(g(\omega, \hat{y})\) - the amplitude spectrum for the elementary signal \(\varphi(t, \hat{y})\). (Line above means statistic average over parameter \(\hat{y}\)). Consequently spectrum of noise of the acoustic cavitation consists of the discrete and continuous components. The fig.1a shows the typical
Spectral characteristics of cavitation noise

Spectrogram of the cavitation noise obtained according to the known method [3] with cavitation being generated in water by the harmonic signal at the frequency of 10 kHz by the amplitude pressure about 2 atm. On the spectrogram the discrete and the continuous components of the spectrum are clearly seen.

In the case of the hydrodynamic cavitation as result of the fact that an exciting wave is described by a random function values \( <N> \) and \( \tau^0 \) (determined accordingly by the amplitude and phase of this wave) are stochastic function. In assumption of statistic independence of these values we have

\[
G_{F1}(\omega) = \frac{<N>^2}{\pi} \left| g(\omega, \nu) \right|^2 \sum_{n=-\infty}^{\infty} \frac{W_n(\tau^0)}{n},
\]

\[
G_{F2}(\omega) = \frac{<N>^2}{\pi} \left[ \left| g(\omega, \nu) \right|^2 - \left| \overline{g(\omega, \nu)} \right|^2 \right] \tau^0^{-1},
\]

where \( <N> = \int <N> W_N(<N>) d<N> \); \( \tau^0^{-1} = \int \frac{W(\tau^0)}{\tau^0} d\tau^0 \); \( W_N(<N>) \) and \( W(\tau^0) \) - the probability density for values \( <N> \) and \( \tau^0 \).

Consequently noise spectrum of the hydrodynamic cavitation turns out continuous.

In some cases it is convenient to model the noise of the hydrodynam-
Spectral characteristics of cavitation noise

Mic cavitation by an acoustic way, generating cavitation by the noise signal with characteristics corresponding to the hydrodynamic pulsation characteristics. Spectrogram of such a cavitation noise is shown on the fig.1b. Cavitation was generated in the conditions similar to the previous ones by using the noise signal with the band width about 4 kHz and the central frequency of spectrum - 10 kHz. It follows from the spectrogram that components $G_{F1}^{h}(\omega)$ and $G_{F2}^{h}(\omega)$ may be distinguished from each other. Such kind of noise is observed by narrow band excitation (for example in the wake current with clearly seen "Karman's path") when components $G_{F2}$ have rather strong pronounced maxima, the positions of which correspond to the periods \( n\tilde{T}_{0} \), where \( \tilde{T}_{0} = 2\pi/\tilde{\omega}_{0} \). It follows from the relations (3) and (4) that in this case the maximum values of the components $G_{F1}^{h}(\omega)$ fall down with increasing of the number $n$ more sharply than the levels of the discrete components of the spectrum $G_{F1}(\omega)$, while the bandwidth of the components $G_{F}^{h}(\omega)$ increasing in the proportion to the number $n$. These conclusions result by comparison of the spectrograms shown on the fig.1.

In case of wide band excitation (for example, in process of cavitation in the developed turbulent current) the components of spectrum $G_{F1}^{h}(\omega)$ and $G_{F2}^{h}(\omega)$ recover each other and their spectral division is impossible.

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The quantum model of the sound wave beam

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The corpuscular and wave presentation of the same phenomenon used in quantum mechanics, can be applied for the solution of several diffractive problems in acoustics of continuous media.

The sound wave beam can be presented as a flux of material particles moving in the potential field of forces. In approximation admitted in geometrical acoustics the sound beams are reduced to the sound rays. The path of these rays are given by eikonal equation and Fermat's rule. The eikonal equation is compatible with the Hamilton-Jacobi equation valid in the classic mechanics and the Fermat's rule is analogous to the principle of minimum energy of a system. The sound ray is then completely modelled through the path of a classical particle.

We have the following pairs of analogous quantities

\[ \xi \leftrightarrow \nu, \quad \eta_{\text{ac}} \leftrightarrow \eta_{\text{ce}}, \quad \gamma \leftrightarrow S \]

where \( \xi \) - sound wave velocity, \( \nu \) - velocity of particle,

\( \eta_{\text{ac}}, \eta_{\text{ce}} \) - the refraction coefficient of sound wave and path of particle respectively, \( \gamma \) - phase shift, \( S \) - generating function.

Passing to the wave approach, it is necessary to take into account not only the path of ray but also the structure of the
The quantum model of the sound wave beam

sound wave beam, namely the finite wave length of this wave. Besides the eikonal equation the equation of flux continuity should be used for the description of a beam:

$$\frac{\partial f}{\partial t} + p \cdot \text{div } \vec{J} = 0$$

(1)

Compatible with the sound beam is the flux of particles to be considered as possessing the finite wave numbers, which means that the particles have the quantum character.

From the time-independent Schrödinger equation, separating its real and imaginary part one obtains the equations

$$\frac{\partial \psi}{\partial t} + \left(\frac{\text{grad } S}{2}m_0\right)^2 + U = \frac{\hbar^2}{2m_0} \psi \quad /2/$$

$$m_0 \frac{\partial \psi}{\partial t} + \text{grad } \psi \cdot \text{grad } S + \frac{\psi}{\hbar} \nabla \psi = 0 \quad /3/$$

where \( \psi \) is the wave function.

The first equation corresponds to the eikonal equation

Introducing the probability density \( \mathcal{J} = \psi \psi^\dagger \) from the second equation follows the relation analogous to (1):

$$\frac{\partial (m_0 \mathcal{J})}{\partial t} + \text{div } (m_0 \mathcal{J} \vec{\nabla}) = 0 \quad /4/$$

The monochromatic sound wave is compatible with the wave packet having the spectral distribution according to the Dirac's function. This is the case of a quasi-classical particle for which \( \hbar \rightarrow 0 \), but \( \frac{\Delta k}{\hbar} \rightarrow 0 \) / k - wave number/. The analogy occurs between:

$$\frac{\Delta k}{\hbar} \leftrightarrow \frac{1}{\hbar} \sqrt{2m_0(E - U)}$$

The wave packet with \( \frac{\Delta k}{\hbar} \neq 0 \) could be compared with the sound signal in a dispersive medium having the phase velocity proportional to the square root of frequency / \( c_p = \text{const } \sqrt{\omega} / \). The velocity of a quantum particle correspond to the group velocity of the sound signals.
The quantum model of the sound wave beam

The quantum particles which would be treated as a model of a sound wave should fulfill the permutation rule \( p^{(p)} |q> = |q> \) and be subject to Bose-Einstein statistics. The spin number \( s \) of such a particle must be an integer. For \( s = 0 \) the flux of particles is a model of a sound field characterized by the scalar acoustical potential, for \( s = 1 \) the flux of the spin particles is compatible with the field of the acoustic vector potential. In the last case the wave function of the particle with the wave vector \( \vec{k} \) is given by the formula

\[
\psi_{k} = \sum_{j} \psi_{j}(k,t) a_{k,j}^{+} |0>
\]

The operator \( a_{k,j}^{+} \) is subordinated to the wave vector \( \vec{k} \), when the creation operator \( a_{k}^{+} \) commonly used in the phonon theory is connected with the scalar \( k \). The flux of the spin particles as a model of sound field is convenient, because it permits to describe all three branches of a sound wave spectrum together.

The sound wave is described through the wave equation and the flux of quantum particle through the Schroedinger equation. In consequence the boundary conditions are in both cases different. The diffraction of a sound wave on the perfectly rigid obstacle is defined by Neumann's boundary conditions \( \frac{\partial \psi}{\partial x} + \frac{\partial \psi'}{\partial x} = 0 \)

The analogous quantum system consists of very high potential barriers for which the Dirichlet's boundary condition \( \psi + \psi' = 0 \) is fulfilled.

The angular distribution of the perturbation wave caused by the obstacle or potential barrier is in both cases given by the series

\[
Q(\Theta) = \frac{1}{e^{\Delta}} \sum_{m=0}^{\infty} (-i)^{m+1}(2m+1)P_{m}(\cos \Theta) \sin \delta_{m} e^{-i \delta_{m}} |q>
\]

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The quantum model of the sound wave beam

for sound wave \( S_m = \arctg \left(-\frac{j_m(ka)}{n_m(ka)}\right) ; \quad q = 1 \)

for flux of particles \( S_m = \arctg \left(-\frac{j_m'(ka)}{n_m'(ka)}\right) ; \quad q = -i \)

The presentation of the sound beam by means of the quantum particles flux is purely conventional. The quantum constant \( \hbar \) has not here any physical meaning. It only defines an arbitrarily chosen way of sound field quantization which indicate the substitution of a continuous system by a discrete one. The admissible energy levels of a quantum particle inside the potential groove correspond to the resonance frequencies of an enclosure. The quantum particles defined in this way could be denominated "macro-phonons", since they have the same properties as the usual phonons, only their quantization constant \( \hbar \) is an arbitrarily one. The formal substitution of a sound wave beam by a flux of "macro-phonons" gives the possibility of a more convenient, approximated solution of some problems of the acoustics of continuous media.

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The Principles of Constructive Mechanics and Acoustics

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Introduction

The constructive mathematics developed by Markov and his collaborators [1] differs from classical mathematics by its general principle of "potential feasibility" and its conception of so-called potential infinity. It means that the mathematical methods may be applied only to processes which may be realized in practice. Such processes allow the descriptions with algorithmic schemes and, therefore, are suitable for computing machine operation.

Markov's scheme of "normal algorithmes" can be stated in the following way. A set of formula

\[ A_i \rightarrow B_i \]

where \( A_i \) and \( B_i \) are some letters or words belonging to an alphabet, orders the substitution of \( B_i \) instead of \( A_i \) if the later is present in a given expression \( P \). This process is closed by final formula

\[ A_k \rightarrow B_k \]

but it can stop when \( P \) will contain \( A_i \) no more. Such formulae or their compositions give a scheme of normal algorithm, the order of operation depending from the sequence of formulae.
Constructive Mechanics and Acoustics

It is possible to develop a new form of theoretical mechanics based on constructive mathematics, which may be used for consideration of different processes in complicated dynamical systems. The possible states of a dynamic system are marked by letters or words in an alphabet or a vocabulary of states. An algorithm in this alphabet defines some feasible transformation of states.

The states of a dynamic system $A$ are expected to be additive in agreement with the principle of Superposition. The addition of such words gives a word belonging to the same vocabulary: therefore these words are similar to vectors in Hilbert's space.

Let a vector of state be designated as $|A\rangle$, a "ket-vector", following Dirac's bracket symbols [2]. The conjugate vector is a "bra-vector" $\langle A|$. The product $\langle A|A\rangle = \langle A|A\rangle$ is a positive scalar. The action of a linear operator $\alpha$ on $|A\rangle$ is given by left side multiplication: $\alpha |A\rangle$. The operator is completely defined if the result of its action is stated. The operator equals zero, when its product with an arbitrary vector is $\{ \}$.

Two linear operators are equal when they give the same results being applied to identical vectors. If any algorithm works according the scheme $|A\rangle \rightarrow |F\rangle$, it may be written the equation: $\alpha |A\rangle = |F\rangle$, where $\alpha$ is an operator corresponding to the algorithm. If there exists such an algorithm $\alpha$, working in the alphabet of vectors $\{ |\alpha\rangle \}$, which satisfies the condition

$$\alpha |\alpha\rangle = \alpha' |\alpha\rangle,$$

where $\alpha'$ is a number, the vector $|\alpha\rangle$ is an Eigen-vector of operator $\alpha$ and the number $\alpha'$ Eigen-value of operator $\alpha$. When the operators commute they have the representation by diagonal matrix form. Let a system of commuting operators be designated by a single letter $\alpha$. Then if $\alpha'$ corresponds to a full set of comut-
ing operators and \( \alpha' \) is a set of Eigen-Values, the representative of an arbitrary ket-vector \( |P\rangle \) will be a function \( \psi(\alpha') \) of \( \alpha' \). So the ket-vector \( |P\rangle \) designated as \( \psi(\alpha') \) gives so called \( \psi \) -function. In the similar way a bra-vector \( \langle P | \) gives a conjugated function, so called \( \psi \) -function.

It seems important to show that the constructive mechanics, based on the theory of algorithms and its formalism, undergoes to the well known form of theoretical mechanics and gives fundamental equations of motion and acoustical wave equations too.

**Equations of motion**

A time-shifted word (vector, operator) is defined by application of an algorithm to the former-unshifted word. Let \( |P_{t_o}\rangle \) be a vector \( |P_{t_o}\rangle \) shifted, \( t_o \) means the initial time. The scheme \( |P_{t_o}\rangle \rightarrow |P_t\rangle \) may be represented by equation

\[
|P_t\rangle = T |P_{t_o}\rangle, \tag{2}
\]

where \( T \) is an unitar operator. The limit for infinitive (in accordance with the constructive principle of "potential feasibility") diminution of \( t - t_o \) of the ratio

\[
\frac{|P_t\rangle - |P_{t_o}\rangle}{t - t_o} = \frac{T - 1}{t - t_o} |P_{t_o}\rangle, \tag{3}
\]

gives a "potential" derivative:

\[
\frac{d |P_{t_o}\rangle}{dt} = \mathcal{H} |P_{t_o}\rangle, \tag{4}
\]

where

\[
\mathcal{H} = \lim_{t \to t_o} \left( \frac{T - 1}{t - t_o} \right).
\]

Using the \( \psi \) function we have:

\[
\frac{d}{dt} \psi = \mathcal{H} \psi. \tag{4}
\]

\( \mathcal{H} \) is a time-shift operator, which is imaginary \([2]\). Considering the time-shifted operator \( \mathcal{U} \), that is \( T \mathcal{U} T \), we find the equation of motion \([3]\)

\[
\frac{d}{dt} \mathcal{U} = \mathcal{U} \mathcal{H} - \mathcal{H} \mathcal{U}. \tag{5}
\]
The Principles of Constructive Mechanics and Acoustics

Equations (4) and (5) transform to well known equations of quantum mechanics if one introduce instead of $\hat{H}$, which is imaginary, a real operator, namely Hamiltonian $\hat{H} = i\hbar \hat{H}$; $\hbar$ is Planck's constant. Then from (4) we have

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad \text{(Schrödinger's equation)}; \quad (6)$$

and from (5):

$$\frac{\partial \Psi}{\partial t} = \{ \Psi, \hat{H} \} \quad \text{(Heisenberg's equation of motion)}; \quad (7)$$

Here $\{ \$, $\}$ is Poisson's bracket. For the stationary state $\hat{H} \Psi = E \Psi$, where $E$ is the Eigenvalue of $\hat{H}$, i.e. energy. In the absence of field (6) gives Helmholtz's equation, often used in acoustics:

$$\nabla^2 \Psi + \kappa^2 \Psi = 0 \quad , \text{where the wave number } \kappa = \sqrt{2mE}k \frac{\hbar^2}{E} \quad . \text{It is obvious that the constructive mechanics is consistent with classical mechanics (when } \kappa \to 0 \text{) also: then (7) undergo to classical Hamilton's equations.}

Results obtained

The methods of constructive mechanics were applied in some acoustical problems: 1) vibrating string loaded with beads and the vibrations of a string net; 2) an acoustical chain with volume elements; 3) a glass road system as an analysing and recognizing device.

References

An Improved Integral Formulation for Acoustic Radiation Problems
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Introduction. We will discuss the numerical solution of the classical acoustic radiation or diffraction problem by means of integral representations. An arbitrarily shaped finite object whose total surface area is \( S \) is immersed in an infinite homogeneous fluid whose density is \( \rho \) and speed of sound \( c \). We consider the steady-state case in which the pressureobeys the Helmholtz equation and a radiation condition in the exterior region \( R_0 \). The region interior to \( S \) will be designated \( R_0^* \). We will consider the Neumann problem in which the normal component of velocity \( v(\xi) \) is known on \( S \).

The integral representation

\[
p(x) = j\omega \int_S \sigma(\xi)e^{-jkd(x, \xi)} \frac{dS(\xi)}{d(x, \xi)}, \quad x \in R_0^*,
\]

is the starting point for the simple-source formulation. The unknown source-density function \( \sigma(\xi) \) is determined by requiring the representation (Eq. 1) to satisfy the Neumann boundary condition, thereby producing the following integral equation:

\[
v(\xi) = 2\pi\sigma(\xi) - \int_S \sigma(\eta) \frac{\partial}{\partial n_\xi} \left( e^{-jkd(\xi, \eta)} \frac{dS(\eta)}{d(\xi, \eta)} \right) dS(\eta), \quad \xi \in S.
\]

Other integral formulations have been based on the familiar Helmholtz integral formulas:

\[
\int_S \left\{ p(\xi) \frac{\partial}{\partial n_\xi} \left[ e^{-jkd(x, \xi)} \right] \right\} dS(\xi) + j\omega \int_S v(\xi) \frac{\partial}{\partial n_\xi} \left[ e^{-jkd(x, \xi)} \right] dS(\xi) = 4\pi p(x), \quad x \in R_0^*,
\]

\[
\int_S \frac{dS(\xi)}{d(x, \xi)} = 0, \quad x \in R_0^*.
\]

The interior Helmholtz integral formulation consists of determining the surface pressure from Eq. 3b and then calculating the pressure field in \( R_0 \) from Eq. 3a.
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Alternatively, in the surface Helmholtz integral formulation the surface pressure is determined from the following limiting form of Eq. 3a:

$$2\pi p(t) = \int_S p(t) \frac{d^2}{d\xi d\eta} \left[ \frac{-i k d(\xi_a, \eta)}{d(\xi_a, \xi)} \right] dS(\xi) = \int_S p(t) \frac{d^2}{d\xi d\eta} \left[ \frac{-i k d(\xi_a, \eta)}{d(\xi_a, \xi)} \right] dS(\xi), \quad \xi \in S. \quad (4)$$

Equation 3a can again be used to calculate the pressure field in $R_o$.

**Existence and Uniqueness of Solutions.** Equations 2 and 4 are two-dimensional Fredholm integral equations of the second kind to which the well-known Fredholm alternative theorems can be applied. It can be shown that for certain characteristic frequencies (or corresponding characteristic wave numbers) non-trivial solutions of the related adjoint homogeneous integral equations exist, and therefore the simple-source formulation and the surface Helmholtz integral formulation do not have unique solutions. This is reasonable on a physical basis since the adjoint homogeneous equations are of exactly the same form as the integral equations for the interior Dirichlet problem for the same object; in fact the characteristic frequencies are the resonance frequencies of the related interior problem.

For these characteristic frequencies, no solution of the simple-source formulation (Eq. 2) exists unless the prescribed velocity function is orthogonal to all solutions of the adjoint homogeneous equation corresponding to Eq. 2. Except for these special velocity distributions the solution of the exterior Neumann problem cannot be represented as a simple-source distribution (Eq. 1). An orthogonality condition must also be satisfied for a solution of Eq. 4 to exist for the characteristic frequencies. However, this condition is satisfied for any arbitrary velocity distribution; therefore, solutions of the surface Helmholtz integral formulation exist but they are not unique. In general the interior Helmholtz integral formulation is not subject to these same difficulties, but it is not well suited for numerical computation.

**Combined Helmholtz Integral Equation Formulation (CHIEF).** An improved integral method is possible because, even at a characteristic frequency, there is only one surface-pressure function which satisfies both Eqs. 3b and 4. The combined Helmholtz integral equation formulation (CHIEF) consists of a practical means of finding this function and using it in Eq. 3a to determine the pressure field. To implement this method we subdivide the surface into $N_S$ mathematical elements and write the square system of algebraic equations which approximates the surface Helmholtz integral formulation (Eq. 4), and then we add $N_I$ equations based on the interior Helmholtz integral formulation (Eq. 3b) for strategic interior points.

The result can be written as

$$J_{ab} F_b = I_{ab} \psi_a; \quad a = 1(1)(N_S + N_I); \quad \beta, \gamma = 1(1)N_S, \quad (5)$$

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where \( p_{\beta} = p(\xi_{\beta}) \), \( v_{\gamma} = v(\xi_{\gamma}) \), and for \( \beta = 1(1)N_{\beta} \) we define

\[
\begin{align*}
\int_{\alpha} = & \sum_{a} \delta_{a} \int_{S_{\beta}} \frac{-d\kappa(x,\xi_{\beta})}{d(x,\xi_{\beta})} dS_{\xi_{\beta}}, \\
& \text{for } x = x_{a} \in S_{\beta} \quad x \leq N_{\beta} \\
& \text{for } x = x_{a} \in R_{\xi_{\beta}} \quad x > N_{\beta}.
\end{align*}
\] (6a)

The subscripted coordinates are reference points on the surface or in the interior of the object. A definition similar to Eq. 6 holds for \( I_{a\gamma} \). These coefficients, which are integrals of known functions, can be accurately calculated by Gaussian numerical quadrature. We solve the non-square, or overdetermined, complex system of equations by a least-square orthornormalizing procedure. Once an approximation of the surface pressure has been obtained by this process, the pressure field can be calculated from a discrete approximation of Eq. 3a.

The uniformly vibrating sphere of radius \( a \) furnishes a simple example of the failure of conventional methods and the success of CHIEF. The characteristic \( ka \)'s, for which no solution of Eq. 2 exists and for which there is no unique solution of Eq. 4, are the roots of the spherical Bessel functions. In this numerical example the surface of the sphere was divided into 4 discrete rings and each ring into 8 sections \( (N_{\beta} = 16) \). The dashed line in Fig. 1 indicates the difference between the numerical answer and the theoretical answer for the surface Helmholtz integral.

\[ \text{Fig. 1. Rel. error in surface pressure vs. } ka \text{ for a sphere} \]

\[ \text{Fig. 2. Far-field pressure magnitude patterns for a box array steered to endfire} \]
formulation ($\mathcal{J}_f = 0$). When one equation was added by utilizing a point at the center of the sphere ($\mathcal{J}_f = 1$), the improvement at and near $ka = \pi$ was dramatic, as shown by the solid line.

Another example is furnished by a 1 by 12 array of electrically steerable transducers mounted flush in one face of an otherwise solid rectangular block of aluminum. A far-field receiving pattern for the array steered to 90° (endfire) was measured in air (so that the aluminum box would appear as rigid as possible). Our previous example illustrated that the influence of a characteristic frequency extends throughout some band of frequencies. For this box-shaped array there were 17 characteristic frequencies within 5% of the frequency of operation. As a result a large and spurious back lobe and other discrepancies appear in the results computed according to the simple-source formulation, as shown by the dashed line in Fig. 2. These disturbing features were also present in theoretical results obtained with the surface Helmholtz integral formulation and even with CHIEF when only a small number of interior equations were used. Because of the density of characteristic frequencies in the region of interest the good results shown by the dots in Fig. 2 were not obtained until 24 interior equations/octant were employed (the surface was subdivided rather coarsely into 67 mathematical elements/octant).

Concluding Remarks. We have explained that the deficiencies inherent for certain characteristic frequencies in the system of equations which approximates the surface Helmholtz integral formulation (Eq. 4) can be overcome by adding equations based on the interior Helmholtz integral formula (Eq. 3b), thereby constituting a combined Helmholtz integral formulation (CHIEF), and we have illustrated the improvement that can be achieved. Presently these techniques are being extended to provide for the analysis of non-rigid structures and for the synthesis of velocity distributions which will produce a desired far-field pattern from arrays of arbitrary shape.
Acoustic Approximation of the Far-Field Blast from Spatially Distributed Explosive Charges
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1. Introduction

The blast wave from a spherical explosion in a fluid medium initially at equilibrium depends upon parameters descriptive of the medium and of the explosion. The classical 'energy hypothesis' (1,2) according to which the explosion is sufficiently characterized by the total energy release, E, together with the assumption that the medium behaves as an ideal polytropic gas, enables properties of the wave to be expressed very simply, any such property \( x \) having a functional dependence of the form

\[
x = x(r, t; E, p_0, c, \gamma)
\]

1. Here, \( r \) represents distance from the charge, \( t \) the time and the medium is completely specified by the three parameters \( p_0, c \) and \( \gamma \), the equilibrium pressure, sound speed and principal specific heat ratio respectively. If \( x \) is expressed in dimensionless form \( X \), we have by the \( \pi \)-theorem:

\[
X = X(\xi, \zeta, \gamma)
\]

2. where

\[
\xi = \left(\frac{E}{p_0}\right)^{\frac{1}{\gamma - 1}}; \quad \zeta = \frac{ct}{r}
\]

and where \( r, p_0 \) and \( c \) have been used as fundamental variables. If \( \gamma \) is assumed constant and if discussion is restricted to properties propagated with the wave, the dependence reduces to:

\[
X = X(\xi)
\]

3. or in the acoustic limit:
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\[ X = \text{const. } \xi \]

Wave amplitude and time scales, for example, are given in the acoustic limit by
\[ \frac{a}{p_0} \left( \frac{\xi}{P_o} \right)^3 \] and \[ \frac{b}{p_0} \left( \frac{\xi}{P_o} \right)^3 \] respectively, \( a \) and \( b \) being dimensionless constants.

2. **Extension of the Energy Hypothesis**

Consider a cylindrical explosive charge of length \( L \), diameter \( D \) and having a uniform explosive density throughout so that upon detonation (assumed to be effected instantaneously throughout the charge) a given constant quantity of energy \( e \) per unit volume is released within the charge. Take a point of observation \( O \) on the produced axis of the charge at a distance \( r \) from its near end. Any property \( x \) of the blast wave at \( O \) thus has a functional dependence: \[ X = x(r, t, L, D, e, p_o, c, y) \].

Applying the \( \xi \)-theorem as before gives for the reduced property:

\[ X = X(\xi', \lambda, \delta, y) \]

where \( \xi' = \frac{\xi}{p_o} \); \( \xi' = \frac{\xi}{T} \); \( \lambda = \frac{L}{r} \); \( \delta = \frac{D}{r} \). The system could be further generalized by assuming \( O \) to be off-axis when an additional parameter would be required. Since this need only be an angle (dimensionless) it would not affect the forms of the other reduced variables. Under the same assumptions as were used in the derivation of Eqn. 3 the dependence of a reduced property becomes:

\[ X = X(\xi', \lambda, \delta) \]

Experimentally, it is found that as \( L \) is increased, the blast waveform separates into two distinct portions associated with the ends of the charge, each portion being then independent of \( L \). When this situation obtains the dependence reduces to:

\[ X = X(\xi', \delta) \]

which may be applied to either part of the waveform (except that when applied to that portion originating at the far end, \( r \) must be reinterpreted as the distance to that end of the charge). In either case the assumption of acoustic conditions, with pressure proportional to \( 1/r \) and characteristic times independent of \( r \), gives from Eqn. 7:

\[ \frac{P}{P_o} = \frac{D}{r} f_1(\frac{\xi}{p_0}); \quad \frac{\theta}{r/c} = \frac{D}{r} f_2(\frac{\xi}{p_0}) \]

where \( p \) and \( \theta \) represent characteristic pressure and time respectively.

We now postulate that the energy hypothesis may be applied to each element of
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an imaginary lengthwise subdivision of the charge. This implies that D and e may be varied in any element, without affecting the form of the blast wave in the far field, provided the variations are such as to keep the energy released in that element constant, i.e. are such as to satisfy \( \delta(D^2e) = 0 \). This condition immediately determines the functions \( f_1 \) and \( f_2 \) as square roots (with appropriate multiplicative constants). Eqn. 8 thus reduces to

\[
p = \frac{a'}{r} \sqrt{\frac{\sigma}{P_0}}; \quad \theta = \frac{b'}{c} \sqrt{\frac{\sigma}{P_0}}
\]

where \( \sigma = D^2e \) is the linear density of energy release and \( a', b' \) are dimensionless constants. These expressions are thus the limiting acoustic pressure and time scaling factors for the blast wave from long uniform linear explosive charges. They may be compared with those for the spherical ("point source") explosions given above.

A similar dimensional analysis may be applied to the case of the more complex linear charge (\( D \) not constant) again applying the energy hypothesis to elementary sections of the charge. In this case we cannot deduce the form of the functional dependence of the wave properties since this depends upon the precise form of the variation of \( D \) along the charge; but we do arrive at the important result that the wave properties depend only (as far as the explosive charge is concerned) upon the linear density of energy release and its space variation, i.e. upon \( \sigma(r) \). This result is analogous to the classical energy hypothesis for point source explosions.

Using this result, any arbitrary 3-dimensional distribution may be reduced, to an equivalent linear distribution. It is only necessary to choose some convenient axis or line-of-sight passing through \( O \) and through or near the charge distribution, and to project the charge distribution isometrically upon it.

3. Acoustic Approximation for the Blast Wave from Linear Explosive Distributions

Each of the elementary sections comprising the linear distribution is assumed to generate a pressure wavelet having the following properties: (i) Independence of all other wavelets, the resultant wave being obtained by linear superposition.

(ii) Spherical symmetry. (iii) A waveform whose shape is similar to that from a small point-source explosion. (iv) An acoustic overpressure/distance law.

(v) Pressure and time scaling factors \( P(\sigma) \), \( \theta(\sigma) \) determined by the dimensional analysis (Eqns 9). (vi) An average velocity equal to the sound speed \( c \).
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With these assumptions the complete pressure waveform from a uniform linear charge may be expressed:

\[ p(t) = F(r) \frac{\sigma(t - \frac{r}{c})}{\sigma(r)} \]

10.

Differentiation of this with respect to \( r \) yields \( dp(t) \), which represents the form of the pressure wavelet due to the element \( dr \) of the charge:

\[ dp(t) = \frac{a_p}{br} \left( \frac{ct - r}{\sqrt{\sigma(r)}} \right) \] \[ \left( \frac{ct - r}{\sqrt{\sigma(r)}} \right) dr \]

11.

For property (iii) we have used a form first suggested by Friedlander (3),

\[ F = (1 - x)e^{-x} \] \[ U(x), \] \[ U \] being the unit function. From assumption (i), the pressure waveform at a point on the produced axis may be obtained by writing \( \sigma = \sigma(r) \) and integrating Eqn. \( 11 \) over the length of the charge, i.e.:

\[ p(t) = \int_{r_1}^{r_2} \frac{a_p}{b} \left( 1 - \frac{ct - r}{b \sqrt{\sigma(r)/p_o}} \right) \exp \left( - \frac{ct - r}{b \sqrt{\sigma(r)/p_o}} \right) U(ct - r) \] \[ dr \]

12.

4. Application to the Simulation of Sonic Bangs

The sonic bang N-wave may be readily simulated using an appropriate linear distribution of explosive (4). The form of \( \sigma(r) \) necessary may be approximated in practice by using detonating fuse. Several strands of this material of appropriate lengths, with ends appropriately offset, are taped into a single bundle to form the charge. Various other linear charges have been developed using this technique and their properties and applications are described elsewhere (5).

5. References


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Distorted Wave Interaction at Boundaries*

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The propagation of a finite amplitude ultrasonic wave leads to the generation of harmonics of an initially sinusoidal disturbance. These harmonics ultimately are established at a specific amplitude and specific relative phase which defines the stable waveform. Certain events, e.g. reflection, can occur in the propagation which cause a change either in the magnitude or the phase of a specific component. When this happens, the propagating medium reacts to reestablish the stable waveform. Whereas the reestablishment of the stable waveform takes place gradually, just as did the initial establishment of the stable waveform, the reflection takes place at a specific position, and therefore causes very little interaction among the Fourier components of the wave. For this reason, we have found it possible to use linear theory to describe the behavior of the individual Fourier components on reflection, even though the amplitude is great enough to require nonlinear theory to adequately describe their behavior as the wave propagates over a distance either before or after reflection. This procedure makes it possible to give a reasonably accurate description of phenomena which are certainly beyond the range of linear theory, but whose complete description would involve hopelessly complicated boundary conditions on nonlinear equations.

To begin with, one can calculate the phase shift which any one of the Fourier components undergoes as it is reflected from the interface. This can be done from classical considerations. The results for water-copper and water-
beryllium interfaces are shown in Fig. 1. The abscissa is the angle of incidence. If one considers each of the Fourier components and assumes that each is phase shifted by the amount obtained from this figure, then the relative phase of the reflected components immediately after reflection gives a measure of the phase shift upon reflection. The data points on this curve are measured phase differences of a reflected distorted wave of fundamental frequency 2 MHz and a pressure amplitude of approximately 0.35 atmosphere which has travelled a distance of 10 cm after reflection.

Now, suppose a wave whose components are phase shifted by 180° is allowed to propagate further. The components will now attempt to rearrange themselves into the stable waveform. A computer program can be used to demonstrate how this takes place. Calculated results are shown in Fig. 2 for the fundamental.

The fact that the distance between transducer and reflector must be given a numerical value prevents the use of the reduced variable $\alpha_0 L$ where $L$ is the discontinuity distance. This is, nevertheless, typical behavior. Only minor changes would be required to satisfy other conditions.

The phase shift of $180^\circ$ is interesting because this particular phase shift results in a reverse smooth waveform, the "least stable" waveform. The nonlinear nature of the medium now causes a decrease in the higher harmonics as the wave propagates away from the boundary. This is shown in Fig. 3 for the second harmonic.

This particular condition is interesting for another reason. It turns out, as can be seen from Fig. 1, that this $180^\circ$ phase shift occurs for liquid-metal interfaces at the angle of incidence for which the slope of the curve is greatest. This is the angle of incidence just beyond the second critical angle at which the reflected beam is found to be displaced along the boundary and one commonly thinks of the generation of surface waves on the reflector. This beam displacement $\Delta$ is given by $\Delta = \frac{2\pi \cos \theta}{\lambda}$ where $\frac{\lambda}{\theta}$ is the slope of Fig. 1, and $\theta$ is the angle of incidence. A plot of this displacement for a 4 MHz fundamental is given in Fig. 4 for water-copper and water-beryllium.

Since this displacement is proportional to the wavelength $\lambda$, to the extent that the reflection of the incident wave can be considered to be a linear process, this reflection will cause the harmonics to be separated relative to each other. The reflection produces a fundamental displaced a distance $\Delta$, a second harmonic displaced $\Delta/2$, a third harmonic at $\Delta/3$, etc.

In practice, this displacement may not be great enough to actually separate the various harmonics into separate beams but it does cause the harmonics to be shifted relative to each other enough to produce unstable waveforms throughout the sound field. The propagation after reflection then is characterized by a
Distorted Wave Interaction at Boundaries

Figure 4. Displacement of 4 MHz beam.

rearrangement of the various harmonic phases and amplitudes toward the most stable waveform.

To demonstrate this, a beryllium reflector was used in water. A 4 MHz ultrasonic wave was incident on the reflector at the angle near maximum displacement of the reflected beam. A scan across the reflected beam was made for both fundamental and second harmonic components at a distance of 20 cm from the reflector. The results are shown in Fig. 5. It can be seen that the second harmonic component, although it is displaced less than the fundamental, is not centered at the position of $\Delta/2$, as would be predicted from the simplified approach. The reason for this is that the second harmonic, being phase shifted by 180° relative to the fundamental, now tends to parametrically amplify the fundamental. Figure 5 was taken at a distance great enough that an appreciable amount of this parametric amplification had taken place. This means that the displaced second harmonic after reflection should decrease in amplitude, then grow again with the phase characteristic of the stable waveform. This effect can indeed be experimentally demonstrated; however, attempts to make quantitative agreement between theory and experiment have until now been unsuccessful. The most likely explanation for this is that the surface waves which are necessarily excited when the reflected beam is displaced are themselves of finite amplitude and produce an unaccounted for effect on the phase and amplitude of the components of the reflected wave.

It is clear, however, that in most cases an adequate picture of reflection from an interface which produces an 180° phase shift can be obtained using this simple model. This phase shift occurs for all angles of incidence on reflection from an interface when the incident (and reflected) wave travels in the medium having the higher specific acoustic impedance. This is true both of fluids and of solids. Two final examples illustrate this.

Figure 6 shows the behavior of an ultrasonic wave after reflection from a water-air interface. The theoretical curves were computed using the computer model; the data points were taken for a 2 MHz wave in the water.

Figure 7 gives the results of a completely different experiment. Pulses of 30 MHz ultrasonic waves were reflected normally from the end of a copper sample. A capacitive detector was used to measure the amplitudes of the harmonic components. Using the amplitudes of the fundamental and either the second or the third harmonics, the value of the third order elastic constant $C_{111}$ could be
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Figure 6. Harmonic content after 180° phase shift.

Figure 7. Third harmonic in a 2.86 cm (100) copper sample calculated when the waves propagated along the (100) direction, since

\[
\frac{A_2}{A_1^2} = k^2 B \left( \frac{3c_{11} + c_{111}}{3c_{11}} \right) \quad \text{and} \quad \frac{A_3}{A_1^3} \approx 2k^4 a^2 \left( \frac{3c_{11} + c_{111}}{3c_{11}} \right)^2.
\]

A specific value of c_{111} = 16 \times 10^{12} \text{dynes/cm}^2 was calculated from direct measurement of the amplitudes of the third harmonic. This led to the dashed line in Fig. 7. After this, the pulse was lengthened until it overlapped itself in the sample. Making the assumption that the 180° phase shift from the end of the sample resulted in cancellation of the harmonics when the pulsed wave train arrived back at the emitting transducer, it could be established that the second harmonic overlapped as predicted from: fundamental = (A + B); second harmonic = (A + B)^2; and third harmonic = (A + B)^3; where A refers to the amplitude of the first received pulse, and B the amplitude of the second received pulse. Increasing the pulse length until three waves overlapped, the signal amplitude became: fundamental = (A + B + C); second harmonic = (A + B + C)^2; third harmonic = (A + B + C)^3. Data have previously been taken on second harmonic generation which agrees with these expressions. The data points in Fig. 7 give the measured signal amplitude of the third harmonic under conditions of overlap indicated. The agreement between the curve and the data points resulting from the assumption about the effect of the 180° phase shift indicates that this technique is not only valuable in bringing signal out of noise for qualitative observations, but is also valuable for quantitative measurements.

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On Surface Resonance Phenomena in the Problem of Surface Scattering

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With the incidence of a plane harmonic wave on periodically corrugated surface there appears in addition to the specular reflection a discrete set of the Bragg spectra. In the case of small corrugations the spectrum amplitudes can be calculated by the small perturbation method, choosing the sum of the incident wave and the wave reflected from a plane surface as the zero-order approximation. However in the case of a perfectly rigid corrugated surface the amplitudes of grazing spectra can acquire a value, which is not small as compared with the incident wave amplitude (surface resonance). In this case the zero-order approximation is to be changed \[L\]. The proposed method has advantage of a greater simplicity and clearness in comparison with other methods used for the solution of the problem by other authors [2-7].

Let a plane harmonic wave

\[ \mathcal{S}_L(x, \varepsilon) = e^{i \beta_0 z} \left[ i (\alpha_0 x - \beta_0 z) \right] \]

impinge on a perfectly rigid periodical surface \[ \varepsilon = \mathcal{G}(x) \] with the period \( L \) and let us assume that \( m \)-th spectrum propagate in the positive direction of \( x \) axis or in the direction near to it so that \( \alpha_m = \alpha_0 + \frac{2\pi}{L} m \equiv \alpha_0 \gamma \)
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where $\mathcal{K}$ is the wave number. We choose now the zero-order approximation in such form as to take account of the main contribution in the full field. As the amplitude of grazing spectrum may be not a small quantity we include $m$-th spectrum into zero-order approximation. Now we choose zero-order approximation in the form

$$ f^{(0)}(x, z) = \mathcal{F}^{(0)}(x, z) + \exp[i(\alpha_n x + \beta_n z)] + \mathcal{M}_m^{(0)} \exp[i(\alpha_m x + \beta_m z)] + \mathcal{A}_m^{(0)} \exp[i(\alpha_m x + \beta_m z)]$$

where $\beta_n = \sqrt{\alpha_n^2 - \lambda_n^2}$, $\mathcal{A}_m^{(0)}$ - the amplitude of $m$-th spectrum. We find the value $\mathcal{A}_m^{(0)}$ from the condition that the full flow of energy into the $m$-th spectrum from other spectra is equal to zero. As the excitation of $nm$-th spectrum has resonant character so is it necessary for calculation of its amplitude to solve the problem in the second approximation in order to take into the account the attenuation of this spectrum due to the scattering.

The scattering field $\mathcal{S} = \mathcal{F} - \mathcal{F}^{(0)}$ satisfies the following boundary condition with an accuracy of square of height of roughness:

$$ \left. \left\{ \frac{\partial \mathcal{S}}{\partial z} \right\} \right|_{z=0} = -\sum_{n=-\infty}^{\infty} R_n \mathcal{F}_n \mathcal{F}_n^* - \left\{ \mathcal{F}_n \mathcal{F}_n^* + \mathcal{M}_m \mathcal{M}_m^* + \mathcal{A}_m \mathcal{A}_m^* \right\} \mathcal{F}_n \mathcal{F}_n^* + \mathcal{A}_m \mathcal{A}_m^* \mathcal{F}_n \mathcal{F}_n^* \right|_{z=0}$$

where

$$ R_n = \frac{l}{4\pi} \int \left[ \frac{\partial^2 \mathcal{F}}{\partial x \partial z} - \frac{d^2 \mathcal{F}}{d x d z} \right] \exp(-i\alpha_n x) dx .$$

The prime above the sum means that $m$-th term is eliminated from this sum.

The field $\mathcal{S}$ equals to the sum of the fields $\mathcal{S}^{(0)}$ and $\mathcal{S}^{(e)}$ produced respectively by velocity sources:

$$ f^{(0)}(x) = \sum_{n=-\infty}^{\infty} R_n \mathcal{F}_n \mathcal{F}_n^* \mathcal{F}_n \mathcal{F}_n^*$$

$$ f^{(e)}(x) = -\left\{ \frac{\partial^2 \mathcal{F}}{\partial x \partial z} + \mathcal{M}_m \mathcal{M}_m^* + \mathcal{A}_m \mathcal{A}_m^* \right\} \mathcal{F}_n \mathcal{F}_n^* + \mathcal{A}_m \mathcal{A}_m^* \mathcal{F}_n \mathcal{F}_n^* \right|_{z=0} +$$

$$ + \left\{ \frac{\partial^2 \mathcal{S}}{\partial x \partial z} + \frac{d^2 \mathcal{S}}{d x d z} \mathcal{F}_n \mathcal{F}_n^* \mathcal{F}_n \mathcal{F}_n^* \right\} \mathcal{F}_n \mathcal{F}_n^* + \mathcal{A}_m \mathcal{A}_m^* \mathcal{F}_n \mathcal{F}_n^* \right|_{z=0} .$$
distributed over the plane \( z = 0 \). The field \( \psi_{\pm}^{(x)} \) is the spectra

superposition with the amplitudes

\[
\mathcal{A}_{n(\pm m)}^{(x)} = -\frac{i}{\beta_n} \int_{-\infty}^{\infty} f(x) \exp(-i \beta_n x) dx.
\]

After integrating in this formula we obtain

\[
\mathcal{A}_{n(\pm m)}^{(x)} = \frac{L}{\sqrt{L^2 - \lambda_n^2}} \left\{ 2 \mathcal{A}_n \left( \beta_o - \sum \lambda_q \right) + \sum_{m=1}^{\infty} \left( \beta_m^2 - \sum_{q=1}^{\infty} \lambda_q \right) \mathcal{A}_m \right\}.
\]

where

\[
\mathcal{A}_n = \frac{i}{L} \int_{-\infty}^{\infty} f(x) \exp(-i \sum \lambda_q x) dx, \quad \sum \lambda_q = \frac{2 \pi}{L} n, \quad \beta_n = \sqrt{L^2 - \lambda_n^2}.
\]

We obtain the amplitude \( \mathcal{A}_n^{(x)} \) from the relation:

\[
\mathcal{A}_n^{(x)} = \frac{L}{\sqrt{L^2 - \lambda_n^2}} \left\{ 2 \mathcal{A}_n \left( \beta_o - \sum \lambda_q \right) + \sum_{m=1}^{\infty} \left( \beta_m^2 - \sum_{q=1}^{\infty} \lambda_q \right) \mathcal{A}_m \right\}.
\]

This amplitude equals:

\[
\mathcal{A}_n^{(x)} = -2 \left[ \beta^{(x)} + \beta^{(z)} \right] \left( \beta_m^2 + \beta_o^2 \right)^{-1}.
\]

where

\[
\beta^{(x)} = i \mathcal{A}_n \left( \beta_o - \sum \lambda_q \right),
\]

\[
\beta^{(z)} = \sum_{q=1}^{\infty} \frac{a_{m,q} \left( \beta_m^2 - \sum_{q=1}^{\infty} \lambda_q \right) \left( \beta_o^2 - \sum \lambda_q \right)}{\beta_m^2},
\]

\[
D = \sum_{q=1}^{\infty} \frac{a_{m,q} \left( \beta_m^2 - \sum_{q=1}^{\infty} \lambda_q \right) \left( \beta_o^2 + \sum \lambda_q \right)}{\beta_m^2} + \beta_m^2 \sum_{q=1}^{\infty} \frac{a_{m,q} \left( \beta_m^2 - \sum \lambda_q \right)}{\beta_m^2} a_{-q}.
\]

We can conclude from these formulas:

1. \( \mathcal{A}_n^{(x)} \) is inversely proportional to the height of corrugation when \( \beta_m = 0 \), \( \beta^{(x)} \neq 0 \);

2. \( \mathcal{A}_n^{(x)} \) in the first approximation is not dependent from the height of corrugation when \( \beta_m = 0 \), \( \beta^{(x)} = 0 \).

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3. $\beta_n^{(c)}$ is proportional to the height of corrugation when $\beta_n \neq 0$;

4. $\beta_n^{(c)}$ is small as compared to unity when $\beta_n \gg 2$, $\beta_n \gg \beta_n^{(c)}$. In this case the formulas for the amplitudes of scattering spectra turn into the corresponding formulas obtained by the small perturbation method when the sum of the incident wave and the wave reflected from the plane surface is taken as zero-order approximation.

The proposed method can also apply for the calculation of sound scattering when two intensive grazing spectra occur.

Literature Cited

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On the sound radiation theory from turbulent flow near an elastic inhomogeneous plate.

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Consider a limited region \( \Omega \) of turbulent flow near a plate. Let us denote as \( S \)-surface of the plate and \( \Gamma \) – the totality of smooth contours, along which the plate has slots. Assume that the slot edges are supported by the elastic ribs. The effect of the slot width and the rib thickness on the acoustic processes in the environment are neglected further. Random processes in the coordinate system related to the plate may be considered as atastically stationary ones. It is assumed formally that random stationary function may be represented by Fourier integral. Only average squares of values have meaning by such formal approach /1/. The spectral amplitudes are given by the equations.

\[
\begin{align*}
\Delta \rho \delta_{ij}(z) + \kappa^2 (1 + i \frac{\partial}{\kappa \partial x_0})^2 \rho \delta_{ij}(z) &= \frac{2}{\partial x_i \partial y_j} T_{ij}(z), \quad \ddot{z} > 0; \\
L \delta_{ij}(z) &= 0, \quad \ddot{z} = 0; \\
M \delta_{ij}(z) &= 0, \quad \ddot{z} = 0, \quad \Gamma^+ O^+, \quad \Gamma^+ O^-; \\
N \delta_{ij}(z) &= 0, \quad \ddot{z} = 0, \quad \Gamma^+ O^+, \quad \Gamma^+ O^-; \\
T_{ij} \approx \rho \nabla \cdot \nabla_0 &; \quad \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}; \\
\n\end{align*}
\]

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\[ L \equiv \left\{ g \left[ \frac{\Delta^s a^s - \kappa^s}{2\sigma_o} \right] \frac{2}{\partial z_o} + \rho_o \omega^2 \left[ 1 + \frac{1 - \beta}{\kappa} \frac{2}{\partial x_o} \right] \right\}; \]

\[ M = \left\{ \left[ \kappa + g \frac{2z_o}{\rho_o (\frac{2z_o}{\rho_o})^2} + g \left( 1 - \rho_o \frac{2z_o}{\rho_o} \right) \right] \frac{2}{\partial z_o} \right\}. \]

Function $P^{(1)}(z_o)$ must satisfy the radiation condition on infinity. Here and further $\kappa = \frac{\omega^2}{C}$, $\rho_o$ is the density, $C$ is the sound velocity in medium at rest; $V_i = \text{flow velocity components}$,

$\sigma; \sigma$ is viscous stress tensor, $\beta$ is Mach number, $\nu$ and $\ell$ are the normal and tangent to the contour $\Gamma$, $g$ is cylindrical rigidity, $\sigma$ is the Poisson coefficient, $K$ - wave number of flexural wave in the homogeneous plate, $Q$ - and $Q'$ - self-conjugate differential operators, produced by the differential expressions in the left parts of equations representing flexural and torsion oscillations of ribs, respectively.

The notations $\Gamma + \mathcal{O}$ and $\Gamma - \mathcal{O}$ mean that slot edges are supported by the elastic ribs. Further we shall call the expression (2) and the radiation condition as boundary conditions, and the expressions (3) and (4) as contact ones.

We introduce function $\tilde{P}^{(2)}(z,z_o)$ which is the solution of additional diffraction conjugate boundary nonstatistic problem. Function $\tilde{P}^{(2)}(z,z_o)$ must satisfy the equation

\[ \Delta^s \tilde{P}^{(2)}(z,z_o) + \kappa^s \left( 1 - \frac{1 - \beta}{\kappa} \frac{2}{\partial x_o} \right)^2 \tilde{P}^{(2)}(z,z_o) = -\mathcal{O}(z-z_o), \quad z > 0, \quad (5) \]

and conjugate boundary and contact conditions. These conditions are described by the formulas (2)-(4), in which the sign before Mach number is changed by the opposite. We shall denote the functions and operators, corresponding to conjugate problem by the wavy line over them. We shall apply the method standard-procedure of Green functions to the equations (1) and (5). Using Green formulas and self-conjugate properties of each of operators $\mathcal{K}$ and $\mathcal{Q}$ (for details see /2/ and /3/) we obtain

\[ P^{(1)}(z) = \int_{\mathcal{Q}} \frac{2z_o}{\partial x_o \partial x_o} \mathcal{T}_{ij}(z_o) \tilde{P}^{(2)}(z,z_o) d\mathcal{O}(z_o). \quad (6) \]
From the eq. (6) it follows that the acoustic field of turbulent flow near the inhomogeneous elastic plate represents quadrupole radiation field. Determine the rib role. For simplicity, consider two dimensional problem. Represent function \( \tilde{\beta}^{(2)}(z) \) as
\[
\tilde{\beta}^{(2)}(z) = \tilde{\beta}_i(z) + \tilde{\beta}_e(z) + \tilde{\beta}_b(z),
\]
where \( \tilde{\beta}_i(z) \) is the incident wave and \( \tilde{\beta}_e(z) \) corresponds to the wave reflected from the homogeneous plate, \( \tilde{\beta}_b(z) \) corresponds to the field, resulting from inhomogeneity (the slots, ribs) in the point with the coordinate, for example, \( \alpha = 0 \). Note that from the boundary condition
\[
\int \tilde{\beta}^{(2)}(z) \, dz = 0, \quad x < 0, \quad x > 0, \quad z = 0,
\]
it follows that
\[
\int [\tilde{\beta}_i(z) + \tilde{\beta}_e(z)] \, dz = 0, \quad -\infty < x < +\infty, \quad z = 0,
\]
and
\[
\int \tilde{\beta}_b(z) \, dz = 0, \quad x < 0, \quad x > 0, \quad z = 0. \tag{7}
\]

Function \( \tilde{\beta}_b(z) \) can be represented as
\[
\tilde{\beta}_b(z) = \frac{1}{2\pi i} \int_{-\infty}^{\infty} \frac{\varphi(\alpha) \exp \left[ i \omega \alpha + i q(\alpha) z \right]}{\sqrt{1 - \beta^2} - \frac{1 - \beta^2}{1 + \beta^2} \alpha} \, d\alpha, \tag{8}
\]
where
\[
q(\alpha) = \frac{\kappa^2}{\sqrt{1 - \beta^2} - \frac{1}{1 + \beta^2} \alpha}.
\]

The choice of radical branch is given by condition \( \Im q(\alpha) > 0 \), when \( \Im \alpha = 0 \). Using boundary condition (7), we obtain the integral equation
\[
\frac{1}{2\pi i} \int_{-\infty}^{\infty} \psi(\alpha) \exp (i \omega \alpha) \, d\alpha = 0, \quad x < 0, \quad x > 0, \tag{9}
\]
where
\[
\psi(\alpha) = \frac{\varphi(\alpha)}{q(\alpha)}, \quad \varphi(\alpha) = \frac{1}{2} \omega^2 (1 + \frac{\beta}{\kappa}) \varphi'(\alpha).
\]

\( \psi(\alpha) \) must be the regular function over the whole plane \( \alpha \).

It is not difficult to show that \( \psi(\alpha) \) is the third power polynomial, i.e.
\[
\psi(\alpha) = a_1 \alpha^3 + a_2 \alpha^2 + a_3 \alpha + a_4, \tag{10}
\]
where \( a_n \) - the factors, which must be determined using contact conditions.
Now we determine a boundary condition for the function \( \tilde{\rho}^{(a)}(z) \).

We have

\[
\tilde{\rho}^{(a)}(z) = \tilde{\rho}^{(a)}_b(z) = \sum_{m=1}^{4} a_m (i \tau \varphi)^m \mathcal{S}(\chi), \quad \infty < \chi < +\infty, \quad z=0.
\]  

(11)

As we see the inhomogenety presence resulted in the occurrence of additional surface sources of aerodynamic noise. The amplitudes of these sources are determined by kind of inhomogenies (contact conditions) and quadrupole radiation field in flow. In particular, it proved for the slot that \( a_3 \approx a_4 \approx 0 \) (see, for example /4/), and for usual support only the dipole term appears to be mantained /5/.

Thus, the inhomogenety presence resulted in additional diffraction effects only in the quadrupole radiation field. However, these changes may be considered as the occurrence of additional sources of turbulent noise applied to the surface of the homogeneeous elastic plate.

It may be shown, that given conclusions are valid for more common case of sound radiation from turbulent flow near the surface of the elastic inhomogeneous shell.

References

Einleitung

Akustische Impedanzen werden meist im Kundtschen Rohr gemessen durch Abtastung der Stehwellen vor dem Meßobjekt. Dieses Verfahren besitzt einige grundsätzliche Nachteile, z.B. den, daß die Schallwelle eben sein muß und daß die Welle nur senkrecht auf die Meßfläche aufgefallen darf.

Grundlage

Es zeigt sich nun, daß man direkt von der Definition des akustischen Leitwerts unter Verwendung der Kraftgleichung zu einem sehr allgemeinen Meßverfahren kommt.

Dazu beschreiben wir den Schalldruck \( p(\bar{r},t) \) eines Schallfeldes beliebiger Geometrie mit der Zeitabhängigkeit \( e^{j\omega t} \) durch:

\[
p(\bar{r},t) = P(\bar{r}) \cdot e^{j\varphi(\bar{r})} \cdot e^{j\omega t}
\]

mit der vom Ortsvektor \( \bar{r} \) abhängigen reellen Amplitude \( P(\bar{r}) \) und dem Phasenfaktor \( e^{j\varphi(\bar{r})} \) mit beliebiger Bezugsphase. Die in üblicher Weise linearisierte Kraftgleichung \( \varphi \frac{\partial \bar{v}}{\partial t} = - \text{grad} \varphi \) lautet für die Komponente \( v_n \) der Schnelle \( \bar{v} \) in Richtung des Normalenvektors \( \bar{n} \)

\[
v_n = \frac{i}{kZ} \frac{\partial \varphi}{\partial n}
\]

mit der Wellenzahl \( k = \omega/c \) und dem Wellenwiderstand \( Z = \varphi c \).
NEUER METHOD TO IMPEDANCE MEASUREMENT

\[ k = \frac{c}{\varepsilon} \]

Dann ist der komplexe akustische Leitwert \( G \) einer Stelle der Messfläche \( S \) gegeben durch:

\[ G = \left. \frac{v_n}{\eta} \right|_{S} = \frac{i}{kz} \left. \frac{\partial \eta}{\partial n} \right|_{S} = \frac{i}{kz} \left. \frac{\partial}{\partial n} \ln \left[ P(\vec{r}) \cdot e^{i \phi(\vec{r})} \right] \right|_{S} \]

\[ = \frac{1}{kz} \left[ -\frac{\partial}{\partial n} \phi(\vec{r}) + j \frac{\partial}{\partial n} \ln P(\vec{r}) \right]_{S} \]

Der Realteil des akustischen Leitwerts folgt somit aus der Messung des Phasenverlaufs des Schalldrucks, der Imaginärteil aus dem Verlauf der logarithmisch registrierten Druckamplitude.

Durchführung des Verfahrens

In der einfachsten Form des Meßverfahrens wird der Schalldruck vor der Meßfläche mit einer bewegten kleinen Mikrophonsonde aufgenommen. Die Sonde muß so angeordnet sein, daß sich die Mikrophonempfindlichkeit bei Annäherung an das Meßobjekt nicht ändert. Mit einem Phasenmesser wird die Phase gegen ein Vergleichssignal (z.B. Summenspannung, Hilfsmikrofon) gemessen und registriert. Die Neigung der Registrierkurve vor der Meßfläche liefert den Realteil des Leitwerts. Entsprechend wird der Verlauf der Druckamplitude vor der Meßfläche auf einem logarithmischen Pegelschreiber geschrieben und die Neigung der Registrierkurve für den Imaginärteil des Leitwerts bestimmt.

In vielen Fällen kann man mit ausreichender Genauigkeit die Tangenten an die Registrierkurven durch Sekanten ersetzen, die an zwei dicht benachbarten Meßpunkten vor der Meßfläche gemessen werden. Dann erspart man sich die Registrierung und kann die Anzeige des Phasenmessers und des logarithmischen Verstärkers direkt in normierten Leitwerten \( GZ \) eichen, wenn der normierte Abstand \( kdn = 2\pi \cdot dn/\lambda \) der beiden Meßpunkte voneinander konstant bleibt. Die Meßgenauigkeit läßt sich dabei erhöhen durch Nullabgleich mit Phasendreher und logarithmischem Abschwächer.
Diskussion des Verfahrens

Einige Besonderheiten des neuen Verfahrens seien im Vergleich zur Kundt'schen-Rohr-Methode (KRM) aufgezählt:

1) Als Grundlage dient neben der Definition des Leitwerts nur die Kraftgleichung (KRM: spezielle Lösung der Wellengleichung im Rohr).

2) Die geometrische Form und die Einfallrichtung der Schallwelle sind beliebig (KRM: ebene Welle, senkrechter Einfall).

3) Die Meßfläche S kann gekrümmt sein (KRM: ebene Fläche).

4) Bei einem Meßobjekt mit Flächenstruktur (z.B. Helmholtz-Resonatoren) werden lokale Impedanzen gemessen (KRM: über den Rohrquerschnitt gemittelte Impedanzen).


6) Daher kann der Absorber im Einbauzustand vermessen werden (KRM: Anfertigung eines Musters für die Messung).

7) Leichte Übertragbarkeit auf Messungen in Wasser (KRM: Herstellung schallharter Rohre schwierig).

8) Auf der Grundlage der obigen Gleichung kann ein direkt anzeigendes Meßgerät relativ einfach entwickelt werden (KRM: komplexes Auswertungsverfahren im Anschluß an die Messung.

Die Meßgenauigkeit des neuen Verfahrens ist dadurch charakterisiert, daß es ein Differentialverfahren ist. Die Genauigkeit ist also am größten, wo sich Phase und Amplitude vor der Meßfläche am stärksten ändern. Das sind die Absorber niedriger Impedanz. In den anderen Fällen ist die Anwendung von Nullabgleichsverfahren mit Phasendreher
und Eichleitung ratsam zur Wahrung der Genauigkeit. Das Verfahren
empfiehlt sich hinsichtlich der Meßgenauigkeit besonders bei Messun-
gen vor nahezu reflexionsfreien Abschlüssen.

Schlußbemerkung

Aus der obigen Beschreibung des neuen Meßverfahrens ergeben sich
eine Reihe von Anwendungsfällen, in denen die Messung im Kundt’achen
Rohr versagt. So läßt sich z.B. der akustische Leitwert an Zylindern
bestimmen [1], die Impedanz bei schrägem Einfall und die Impedanzver-
teilung an der Oberfläche strukturierter Absorber läßt sich ermitteln.
Es bietet sich auch die Möglichkeit an, Wirkleistungsdichten (Schall-
intensitäten) \( N_{\text{eff}} \) zu messen, da diese in einem beliebigen Schall-
feld einer harmonischen Welle gegeben sind durch

\[
N_{\text{eff}} = \frac{1}{2} p^2(\tau) \cdot \text{Re} G.
\]

Bei der Verwendung des obigen Verfahrens zur Messung von \( \text{Re} G \)
erhält man die Komponente des Wirkleistungsvektors in der Meßricht-
zung \( \vec{n} \) des Normalenvektors der Meßfläche \( S \). Es ist grundsätz-
lich gleichgültig, ob in einem rein fortschreitenden Wellenfeld oder
in einem Stehwellenfeld mit mehr oder weniger hohem Reflexionsanteil
gemessen wird. Damit könnte man also z.B. die abgestrahlte Leistung
eines Senders oder die absorbierte Leistung eines Absorbers in einer
reflektierenden Umgebung ermitteln.


Axial geführte Oberflächenwellen an Zylindern mit komplexer
Impedanz.
Subsonic Atmospheric Oscillations

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Introduction

The passage of a jet stream in the atmosphere over the eastern (Atlantic) seacoast of the United States is occasionally accompanied by large oscillations in barometric pressure at infrasonic frequencies. The periods of oscillation are usually greater than five minutes, and the pressure fluctuations at the earth's surface are mainly greater than 150 dynes/cm².

The jet stream is a thin layer of fairly high speed wind. The location of the layer in the atmosphere is in the neighborhood of the tropopause, at an altitude of about 10 km. The thickness of the stream is about one kilometer. The wind speed along the axis is frequently 30 meters/sec, and sometimes as great as 80 meters/sec. The wind blows towards a direction between northeast and southeast, and the width of the stream (in a direction transverse to the direction of flow) is generally at least 100 km.

The oscillations in barometric pressure, hereinafter referred to as "sound pressure", are measured by means of line-microphones located on the ground. The Washington station of our laboratory has an array of four such microphones located at ground level and spaced about 5 - 10 km apart. Each line microphone produces frequency-modulated voltages proportional to the sound pressure in the atmosphere. The voltages are transmitted by telephone wires to a recording location. Here they are demodulated, amplified and filtered, and recorded in analog form both as

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ink-on-translucent-paper traces, and on magnetic tape. An important feature of the recordings is the provision of accurate timing schemes.

The microphone array at the station is currently designed for the measurement of four principal characteristics of infrasonic waves. These are (1) the amplitude and waveform of the incident sound pressure, (2) the direction of propagation of the wave, (3) the horizontal phase velocity, and (4) the dominant period (or periods) of oscillation.

The results of observations made at our station in Washington show that almost all sound waves coming from subsonic oscillations of the jet stream have wavefront surfaces of constant phase which are almost plane. The sound pressure has the following features when the jet stream is blowing. (1) The direction of propagation of lines of constant-phase sound pressure across the Washington area is very close to the direction of the jet stream over Washington. (2) The horizontal phase velocity \( c_o = 10 \) to \( 100 \) m/sec is about the same as the speed of the jet. (3) The sound pressures are mainly in the range \( 50 - 400 \) dynes/cm\(^2\). (4) Periods of oscillation \( T = 250 \) to 1000 seconds.

The sound pressure probably has its origin in flow instability of the jet stream. The mechanism of the instability is not known. We can conjecture that it arises from a combination of viscous shear between the jet stream and the surrounding atmosphere, and unstable temperature gradients. We assume that the jet stream oscillations force the atmosphere into oscillation. The purpose of the investigation is determination of the relationship between the measured sound pressure and the oscillatory displacements of the jet.

Equations of Atmospheric Motion

The well-known equations of motion for sound waves in a wind-free atmosphere, see for example Reference (1), are presented here subject to the following conditions. (1) The atmosphere is isothermal and wind-free. (2) The waves are sinusoidal in time, and all quantities vary like \( \exp(i\omega t) \). (3) All motions are in the x-z plane, and so the particle velocity, with components \( u, v, w \), has its y-component \( v = 0 \), see Figure 1. (4) The traces of the straight lines of constant-phase sound pressure on the x-y plane have a phase velocity \( c_o = \omega/k_o \), and so all
Fig. 1 Radiation of sound pressure by jet stream oscillations

quantities vary like \( \exp(-ik_0x) \); the waves are advancing in the (+x) direction. The
equations of motion reduce to

\[
\frac{\partial}{\partial x} \left( \frac{\partial u}{\partial x} \right) + \frac{\partial w}{\partial x} + k^2u - \left( \frac{\rho \partial^2}{\partial x^2} \right) \frac{\partial w}{\partial x} = 0
\]

\[
\frac{\partial}{\partial z} \left( \frac{\partial u}{\partial x} \right) + \frac{\partial w}{\partial z} + k^2v - \left( \frac{\rho \partial^2}{\partial z^2} \right) \frac{\partial w}{\partial z} - (\gamma - 1) \left( \frac{\rho \partial^2}{\partial x^2} \right) \frac{\partial u}{\partial x} - \frac{\partial w}{\partial z} = 0
\]

with the boundary condition \( w = 0 \) at the xy-plane. \( \gamma = 1.40 \) for the atmosphere,
\( c = \) velocity of sound = \( \omega/k \), and \( g = \) the acceleration of gravity. The components
of particle velocity, \( u \) and \( w \), vary with \( x \) like \( \exp(-ik_0x) \), and with \( z \) like \( \exp(kz) \).

\[
u = u_0 \exp(-ik_0x + kz)
\]

\[
w = w_0 \exp(-ik_0x + kz)
\]

Introduction of these expressions into the equations of motion leads to a quadratic
equation in \( \beta \), from which the allowed values of \( \beta \) are given by

\[
\beta = \frac{1}{2} \sqrt{\frac{\gamma - 1}{\gamma} \frac{k_0^2}{\kappa^2} - \frac{\beta^2}{\rho} \left( \frac{k^2 + \kappa^2}{\gamma} \right) - \frac{\lambda^2}{\rho}}
\]

where \( \kappa = \) scale height of the atmosphere = \( c^2/\gamma g \).

As we shall see a little later in the discussion, \( \beta \) is a real number for a
typical subsonic oscillation. Hence, the atmosphere between the jet stream and the

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Subsonic Atmospheric Oscillations

ground is traversed by both upward-going and downward-going waves, combined so as to have \( w = 0 \) at the ground. The final expression for \( w \) is

\[
w = w_0 \sin(\beta z/H) \exp(z/2H - ik_0 x)
\]

From this we see that the oscillatory amplitude of \( w \) increases exponentially with altitude. The increase is inversely as the square root of the ambient pressure.

The coefficient \( w_0 \) can be computed from the measured sound pressure at the ground level, \( z = 0 \). The sound pressure is

\[
P_0 = \frac{-i B}{hw} \left( \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z} \right), \text{ at } z = 0.
\]

Combination of the expressions for \( w \) and \( P_0 \) with the equation of motion gives the following expression for the amplitude of the vertical component of particle displacement at the 10 km altitude of the jet stream:

\[
\Delta z = 2H(k^2 - k_0^2)|P_0|/8\pi B k^2
\]

As an example, consider a wave with \( T = 500 \) secs, \( c_0 = 33 \) m/sec \((=c/10)\), and \( |P_0| = 200 \) dynes/cm\(^2\). We find \( \Delta z = 60 \) meters, which must be the jet stream's vertical oscillatory displacement at an altitude of 10 km necessary to produce the measured sound pressure at the ground.

The jet stream presumably radiates sound pressure towards the upper atmosphere as well. The details of this radiation remain to be worked out.

References

Exciting Surface Waves in Liquid by Ultrasonics

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**Introduction.** A scheme is given for the conversion of longitudinal vibration of the piston into transverse waves on the liquid surface. Wave can be visually observed.
The tray (Fig. 1) is filled with water that the piston is half submerged. When the high frequency oscillator was switched on, an impulse travelled along the water surface. If the anode circuit was broken automatically (for instance with relay P), transverse waves travelling along the water surface, could be very well observed with naked eyes.

![Diagram of apparatus for obtaining surface waves with ultrasonics](image)

Fig. 1. Schematic diagram of the apparatus for obtaining the surface waves with ultrasonics.

The ultrasonic frequency used in the experiment was equal to 1 megahertz, and 500 Volts were fed to the piston. Relay actuation frequency was 1 hertz.

The measurements showed that under the given conditions, the phase velocity of wave was of the order \( v = 0.5 \text{ cm/sec} \).

The waves generated in this manner can be obtained in any form depending on the nature of modulation.
On the Velocity Distribution of Flow Along the Piston Axis

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Introduction. A method is given to observe the velocity distribution of the flow along the ultrasonic piston axis. Maximum is found for the flow velocity.

Fig. 1 shows the apparatus designed to observe the velocity distribution of a flow along the piston axis.

The cylindrical tube AB, 8 cm in diameter and 100 cm in length, ends in a 50 cm tapered nozzle to damp the reflected waves.

A 3 cm x 100 cm observation window was cut on the cylindrical part of the tube. A quartz plate, 25 mm in diameter, was used as the piston, which was excited at a natural frequency of 1.2 megahertz.

The piston was located at the fore end of the cylindrical tube at the point A (Fig. 1). Exciting voltage, of the order of 0.5 kV, was fed from a master oscillator through a
single-cascade power amplifier $Y$.

A weak aqueous solution of paper developer (3.5 l water + 0.5 l usual developer) was used as the liquid.

1 cm x 12 cm narrow strips of previously exposed photopaper were placed at different points along the piston axis. The plane of photopapers were placed in the direction of wave propagation as shown in Fig.1. Acoustic waves generating the acoustic flow were excited in the medium. Since the flow velocity was supposed to be different at different points, the rate of blackening of each photopaper should be different.

The development time for the paper (with a developer concentration No.7 and No.4) varied from 5 to 10 minutes. By making use of photometer, we could succeed in determining the intensity of blackening at the investigated points along the piston axis. The measurement results are shown in Fig.2, in which the distance from the piston is plotted against x-axis, and blackening of paper proportional to flow rate against y-axis.

From the curve, it is obvious that the flow rate varies along the x-axis, and the maximum occurs at 20 cm from the piston.
High energy neutron detection from cavitation in water

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Recently, some of us\(^1\) have investigated the possibility of neutron detection and dosimetry by means of ultrasonic cavitation in water. The experimental set-up consists of a large container from which water is drawn through a long pipe into the test cell. Here ultrasound acting on the liquid can produce cavitation at a suitable sound intensity. A statistical treatment\(^2\) allows the calculation of nuclei concentration as a function of the acoustical pressure required for their growth.

If the liquid, has been exposed to neutron irradiation along the pipe, the nuclei concentration changes, and the difference can be attributed to nuclei created by the incoming neutrons.

In the above mentioned work a Ra-Be neutron source was used. Neutron energy, in such a case, was lower than 14 MeV. Because the nucleation process is due to ionizing knock-on nuclei, and because the energy that a neutron can give to struck nuclei depends on the mass ratio, it is possible, by adding compound with suitable atoms to make the water under test sensitive to different neutron energies.

It was shown that oxygen nuclei are rather poor nucleating agents with Ra-Be neutrons. On the other hand the addition of light elements, as Li, B, C, strongly enhances the effect of neutron irradiation.

—H-229—
In fig. 1 we report the conclusions of this work. On the left the concentrations of nuclei produced by neutron irradiation is given for the variously doped water sample. On the right the theoretical distributions are shown.

In the same conditions a check was performed in which a potassium salt was added to water. No appreciable effect was detected in this case, as a consequence of the large atomic mass of the potassium.

In the present work we report some preliminary results with the same technique and a neutron beam of very high energy.

The water under test was irradiated by neutrons emerging in photo-reaction induced by the γ-beam of an Electron-Syncrotron (Prascati, Rome). The energy of the beam was 900 MeV and neutrons are created in a range of energy from 25 MeV up to 900 MeV, the total flux of neutrons can be evaluated at $5 \times 10^6$ neutron sec$^{-1}$. The neutron energy spectrum is approximately of the form

$$n(E) = \frac{A}{E^{-\alpha}} + \frac{B}{E^{-\beta}}$$

with $\alpha \approx 2$ and $\beta \approx 7$.

In fig. 2 we report the statistic of cavitation events for pure water (left hand side) and the corresponding nuclei distribution function (right hand side). A characteristic feature is evident: cavitation events occur in a narrow sound pressure interval, due to high nuclei population created by oxigen recoil nuclei. In other
High energy neutron detection from cavitation in water

Fig. 2 Statistic and nuclei distribution in pure water

Fig. 3 As fig. 2, in potassium solution

Fig. 4 Difference between pure water and potassium solution

words, for neutron energy we use, oxygen are largely in condition to nucleate.

On fig. 3 report analogous results obtained with water in which a potassium salt was dissolved.

Fig. 4 shows the difference of the two preceding curves. Such a difference represents large nuclei created by potassium knock-on nuclei. Potassium therefore acts as a good nucleating agent with the high energy neutron of the present experiment.
High energy neutron detection from cavitation in water

Some conclusions can be drawn from such results:

1) The experimental results agree with the theory of the nucleation process developed previously i.e. the process is due to knocked-on atomic nuclei. Oxygen and Potassium nuclei that do not nucleate cavitation for neutron energy up to 14 MeV in the used set up produce a large nuclei population with neutrons of higher energy.

2) The minimum value of acoustical pressure at which the effect of irradiation shows up is, however, of the same order of magnitude as the value obtained with 14 MeV neutron (see ref. 1). In addition there is no difference in the lower limit of acoustic pressure needed for cavitation between the two cases in which oxygen or potassium atoms acts as nucleating agents.

This means that an upper limit seems to exist for the size of a cavitation nucleus. In fact one aspect is that microbubbles created by potassium would be larger than those created by oxygen, as a consequence of the larger specific energy loss of the first one. Analogously nuclei created by oxygen would be larger than those created by e.g. boron or carbon nuclei.

It is possible that the size limitation is due to the stabilizing process.

3) The neutron detection method we use do not allow a detailed and complete investigation of neutrons spectrum. Our method, in fact gives information only on the population of larger nuclei, a small number of which is sufficient in our experiment to trigger cavitation at each test and therefore do not make it possible to examine the content of smaller nuclei. Such a method maintains its validity only for very small fluxes of neutrons and becomes inefficient for large fluxes.

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Ultrasound Absorption in Mixtures of Helium, Neon and Argon
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The attenuation of 71 kHz sound has been measured at 24°C in mixtures of helium and argon to which neon is added in progressively increasing amounts. The measurements are made by the so-called direct method, in which a pulse-modulated signal from a vertically movable sender is picked up by a fixed receiver in a cylindrical vacuum-tight metal tank 50 cm in diameter and 125 cm long.\textsuperscript{1,2} A block diagram of the measuring system is shown in Fig. 1.

The received signal is shown on an oscilloscope after passing through an attenuator. As the distance between the sender and receiver is varied, the intensity of the received signal varies, but the height as indicated on the oscilloscope is kept constant by adjusting the attenuator, whose readings are then used in computing the observed attenuation.

The sender is equipped with a tapered end to assure that the wave form of the emitted radiation is spherical to within 1%. The practical range
Ultrasonic Absorption in Mixtures of Helium, Neon and Argon

of sender-receiver separation, controlled by the echoes in the tank, turned out to be from about 10 cm to 40 cm. The usable pressure range extended from 35 mm Hg to 90 mm Hg, and in this range $ap/f^2$ remained constant to within the experimental error. Here $p$ is the gas pressure, $f$ the frequency and $a$ the attenuation coefficient. This pressure range corresponds to an angular frequency ratio to pressure ($\omega/p$) range from 3.75 MHz/atm. to 9.4 MHz/atm. The stated purities of the gases used were: argon (99.996%), helium (99.93%) and neon (99.998%). The overall error in $ap/f^2$ from all sources is estimated at about 6%.

In carrying out the experimental measurements the He–Ar mixtures corresponded to the six mole fraction ratios of helium to argon 0.1/0.9, 0.3/0.7, 0.5/0.5, 0.6/0.4, and 0.8/0.2. To each of these mixtures neon was added to bring its molar percentage of the total mixture to 5%, 15%, 25% and 33 1/3%. The basic results are presented in Fig. 2, which indicates $ap/f^2$ for each of the 30 mixtures studied. For convenience the experimental points corresponding to the same amount of neon in the mixture are connected by a smooth curve, which then presents $ap/f^2$ as a function of the helium-argon mole fraction ratio. All curves in question are plotted on the same diagram by shifting the origin appropriately up the ordinate axis. The top curve (for 0% Ne) is that obtained by Law et al., and is inserted for reference. The curves show that as the percentage of neon in the total mixture is increased, the absorption gradually decreases for each helium-argon mole fraction ratio. Moreover the curves become flatter and $(ap/f^2)_{\text{max}}$ shifts from a He–Ar ratio of 0.5/0.5 for 0% Ne to 0.6/0.4 for 33 1/3% Ne.

The decrease in absorption is shown more vividly in Fig. 3, in which the difference between the curve of Law et al. (for 0% Ne) and the four other curves of Fig. 2 is plotted. As the percentage of neon increases the difference progressively increases, with its maximum occurring in the region in which the helium and argon concentrations are about equal. The effect of the neon on the absorption appears to be negligible for the extreme He–Ar mole fraction ratios.

The theoretical calculation of sound attenuation in ternary mixtures is formidable. Hence the results of the measurements reported here are given a tentative
phenomenological explanation. It is plausible to attribute the observed decrease in attenuation with addition of neon to either the effect of viscosity and heat conduction (classical absorption) on the one hand or to that of diffusion on the other or a combination of both. From the observations of Petralia, one would expect that the addition of neon to the helium-argon mixture would increase the attenuation due to classical absorption, with the largest increase taking place when the He-Ar ratio is high. Since our observations indicate that the total attenuation decreases with increasing addition of neon, it appears that the increase in classical absorption is in most instances offset by a larger decrease in absorption due to diffusion; that is, the larger the amount of neon added, the smaller becomes the diffusion effect associated with the relatively large difference in molecular weights of helium and argon.

An additional justification of this conclusion comes from further examination of Fig. 3. The greatest difference between the curve of Law et al. and our experimental curves occurs at the middle range of He-Ar mole fraction ratios, i.e., between 0.3/0.7 and 0.7/0.3. It is precisely in this region that the attenuation due to diffusion is the largest and, so to speak, capable of decreasing more, even though the percentage decrease in this attenuation may still remain constant. This decrease cannot be compensated for by increases in the attenuation due to viscosity and heat conduction. At the extremes of the He-Ar ratio, where attenuation due to diffusion is smallest, a smaller decrease in this attenuation can now be balanced by greater increases in classical attenuation, with the net result of
approximately zero change, as shown.

References


The Temperature Dependence of the Rotational Relaxation Time in Gases.

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Introduction

We have been studying the rate of equilibration of the rotational degree of freedom in hot gases for almost three years now, and I would like to take this opportunity to review our findings. Briefly, these findings have been as follows:

1) We have examined more than seven gases, both diatomic and polyatomic, and in every case the rotational contribution to the specific heat attains its equilibrium value more slowly at high temperatures than at low. This is not to say that the rate constant for transitions between specific rotational levels necessarily decreases; on the contrary, even though the specific rate constants are increasing with temperature, the equilibration of the total rotational specific heat will still be slower. 2) This effect of the equilibration becoming slower at high temperatures is more pronounced in molecules with large moments of inertia. 3) This anomalous temperature dependence is completely explained by the increase in spacing between energy levels with increase in the rotational quantum number. Rotational equilibration is fundamentally a multiple relaxation process and if one insists in describing it with a single time constant, one is faced with the improbable situation of a reaction which goes more slowly at elevated temperatures. If, on the other hand, one recognizes that each transition has its characteristic relaxation time, the time being greater the larger the energy gap, then one interprets the slower
The Temperature Dependence of the Rotational Relaxation Time in Gases

overall equilibration at high temperatures as being due to the large spacings between the levels which are occupied at the high temperatures. Being creatures of habit, it has been natural for us to take terms like "relaxation time" and "collision number" from vibrational relaxation theory and apply them to rotation. I hope to convince you here that this practice is both incorrect and misleading.

I would first like to present some typical experimental results. Then I would like to describe a calculation we have made which embodies the multilevel nature of a rotating diatomic molecule and which completely accounts for the observed behavior.

Experimental Results

Let me begin with normal hydrogen at room temperature as shown in slide 1. We have plotted the velocity squared and the molecular absorption of 1 MHz sound versus the frequency/pressure ratio. The circles are the experimental points and the solid line is single relaxation theory with the relaxation time chosen to best fit both the absorption and the velocity data. As usual, the maximum of the absorption curve and the inflection point of the velocity dispersion curve occur near the frequency at which \( \omega t = 1 \). The next slide at 800°C shows that the relaxation frequency has shifted from about 13 MHz to perhaps 5 MHz which corresponds to the relaxation time increasing from \( 1.5 \times 10^{-8} \) to \( 5 \times 10^{-8} \) seconds as the temperature was raised.

Next I would like to show you the behavior of a molecule with higher moment of inertia, nitrogen. The next slide shows \( N_2 \) at room temperature and we see very little dispersion because we know from other investigators that the relaxation frequency is higher than 300 MHz. In the next slide at 800°, the relaxation frequency has shifted to about 50 MHz, a shift of about 300 MHz over the same temperature range which caused \( H_2 \) to shift 8 MHz.

As a final example, the next slide shows methane at room temperature. It is known from other investigators that there is a vibrational relaxation at about 70 KHz and a rotational relaxation at about 300 MHz, and both of these are beyond the range of our instrument. At 300°C, as shown in the next slide, the vibration has moved up while the rotation has moved down and both dispersions are visible. By
The Temperature Dependence of the Rotational Relaxation Time in Gases

500°C, as seen in the next slide, the dispersion is almost continuous and the two absorption peaks may be seen. This case provides clear evidence that the temperature coefficient of the equilibration time for vibration and rotation have opposite sign.

Theoretical Explanation

Now for the explanation of this odd behavior of rotation. We have chosen a hard sphere model of a colliding system in which all molecules which come within a distance \( \sigma \) of each other are considered to collide. We assume that all collisions which take place result in a single transition probability \( p \), so long as there is sufficient kinetic energy in the collision to bridge the energy gap between the given rotational energy levels. Under these assumptions, one finds for the rate constant:

\[
k_{ij} = N(\pi \sigma^2 p)(8kT/\pi \mu)^{1/2} \exp(-\sigma^2 \Delta E_{ij}/kT)
\]

where \( N \) = number of molecules/cm³

\( \pi \sigma^2 p \) = effective collision cross section. It is evaluated by fitting room temperature velocity data.

\((8kT/\pi \mu)^{1/2}\) = mean relative velocity

\( \sigma \) = an adjustable constant to adjust for the fact that all energy collisions are not equally likely to produce a change in level. \( \sigma \) is determined by comparing \( \text{H}_2 \) and \( \text{D}_2 \) experiments in which \( \pi \sigma^2 \) is taken to be same for each.

\( \Delta E_{ij} \) = energy spacing between levels \( i \) and \( j \)

Note that temperature appears in this rate constant equation in both the coefficient and the exponent. At unit pressure and volume, \( N=1/kT \) which would make the rate constant decrease with increasing \( T \). Temperature also appears in the exponent in such a way as to make the rate constant increase with \( T \). This is reflected in the next slide which is a tabulation of \( k_{ij} \) for \( \text{H}_2 \) and \( \text{D}_2 \) at three temperatures. For both systems the rate constants for transitions between the lower rotational states decrease with temperature while for higher transitions, the rate constants increase. The concentration term dominates in the low lying states.
while the exponential term dominates the higher levels. Note also that at any
given temperature, the rate constants decrease as the energy gap gets larger.

The manner by which these rate constants are translated into a velocity dis-
persion curve is quite involved and not germane to the point I would like to make
here. As an indication of the difficulty of the calculation, it might be noted
that if there are N levels to be considered, the calculation involves solving N
coupled differential equations and the nitrogen calculation alone required over 200
hours on our IBM 7040. The calculation reflects great credit on Professor Raff who
is responsible for all the theoretical work presented here.

The next slide shows some of the results of this calculation. The circles are
the experimental values of the ultrasonic velocity of room temperature hydrogen
and the solid line is the theoretical curve. Of course the collision cross section was
adjusted to make the curve fit the data but the shape of the curve seems correct.
The next slide shows the same data for 873 °K . . . . . . and the next slide shows the
same data for 1073 °K. The shift in the inflection point with temperature is
clearly being reproduced.

The next slide gives the results for N₂ at 293 ° . . . . . and the next slide
gives the results for N₂ at 1073 °. Again, the shift in the dispersion curve is re-
produced in N₂ with its large moment of inertia. The shift in the inflection point
of the deuterium data is also very well predicted by this model.

Having a model which reproduces accurately the temperature dependence of the
ultrasonic dispersion, we may now investigate the origin of this dependence. It
might be supposed that the shift is a result of the decrease in rate constant with
temperature for low J. Since k₀₁ exhibits the largest decrease, a two state model
using this rate constant should produce the largest shift and the next slide shows
this model fitted to the room temperature H₂ data. The next slide shows this model
at 873 ° . . . . . . and the next slide shows this model at 1073 °. While there is some
shift, it is clearly not enough. We may conclude that the frequency shift of the
velocity dispersion with T is not indicative of a decrease in the associated rate
constants.

On the contrary, the temperature dependence is due to the multilevel nature of the
rotational energy. This is clearly shown in the next slide which gives the
dispersion curves for H₂ at 800 °K as a function of N.

Conclusion

We hope that we have demonstrated to your satisfaction that the shift of the
absorption maximum and the dispersion inflection point to lower frequencies with
increasing temperature is not directly associated with the temperature dependence
of the rate constants. We also hope that the next time you are tempted to say
"rotational relaxation time" or "zip" you won't.

This work was supported by the G.S.U. Research Foundation, The U. S. Army
Research Office Durham and by N.A.S.A. More information on the work presented may
be found in:
Hill & Winter, J. Chem. Phys. 49, 0000 (1968)
Low Frequency Sound Attenuation in Gases and Gas Mixtures

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The method used was essentially similar to that employed by Harlow and Kitching (1964), but the speed and accuracy of curve plotting and subsequent calculations were improved by using a Ferranti Sirius computer. A plane diaphragm was driven at constant amplitude and excited a gas column confined by a cylindrical tube and terminated at its other end by a massive reflector. The tube material was duralumin, 11.5 cm in diameter and 170 cm long. Measurements were made between 100 Hz and 1200 Hz.

The equation to the variation with frequency of the impedance of the diaphragm-gas column system may be written

\[ D^2 \hat{Z}^2 = 1 + D^2(s^2 + t^2) + 2Dm(D^2t^2 + 1)^{\frac{1}{2}} \cos g \]

\[ -\left( \frac{2}{\cosh 2\alpha_0 - \cos 2\pi n(\frac{f}{\tau_n} - 1)} \right) \left\{ \sin g \sin 2\pi n(\frac{f}{\tau_n}) - 1 + \frac{1}{D^2t^2 + 1} \right\} \]

\[ + \left( \frac{1}{\cosh 2\alpha_0 - \cos 2\pi n(\frac{f}{\tau_n} - 1)} \right)^2 \left\{ \sin^2 2\pi n(\frac{f}{\tau_n}) - 1 + \frac{1}{D^2t^2} \right\} \]

where \( Z \) is the measured driving point impedance

\( D \) is a parameter for conversion to fundamental units

\( s \) is the height of the mid point of the curve of impedance plotted against frequency

\( t \) is half the difference between the maximum and the minimum of the
impedance curve

g is the angle between the line from the centre of the circle representing the total impedance variation in an Argand diagram to the point representing the impedance of the diaphragm, and the initial line

a is the attenuation in the gas column

l is the length of the gas column

\( f_n \) is the frequency of the \( n \)th mode of the gas column.

The computer was used to determine the values of the quantities \( D, a, s, t, g \) and \( f_n \) to obtain the best fit with the experimental data. The attenuation was then determined from \( \sinh 2al = 1/Dt \). The relaxation attenuation is \( a_R \), given by

\[
\frac{f^2}{a_R} = \frac{V}{n} \cdot \frac{C^p_C^\infty}{RC_1} \cdot \frac{f_0}{f_0^2 + f^2}.
\]

where \( v \) is the velocity, \( f_0 \) is the frequency of maximum absorption, \( C^p, C^\infty \), refer to infinite frequency and \( C_1 \) refers to the internal mode. If \( S \) is the slope of the linear plot of \( f^2/a_R \) against \( f^2 \) and \( I \) is the intercept on the axis of \( f^2/a_R \), we have \( f_0 = (I/S)^{\frac{1}{2}} \).

Pure gases

The attenuation was measured in \( N_2, O_2 \) and air free from \( CO_2 \). In each case the highest purity commercial gas was used and corrections were made for residual foreign gases. The attenuation was found to be proportional to \( (f/p)^{\frac{1}{2}} \) for each of the gases investigated. The slopes of the lines were:

\[
\begin{align*}
N_2 & \quad 0.550 \times 10^{-4} \text{ cm}^{-1} \text{ Hz}^{-\frac{1}{2}} \text{ cm Hg}^{\frac{1}{2}} \\
O_2 & \quad 0.578 \times 10^{-4} \text{ cm}^{-1} \text{ Hz}^{-\frac{1}{2}} \text{ cm Hg}^{\frac{1}{2}} \\
Air & \quad 0.563 \times 10^{-4} \text{ cm}^{-1} \text{ Hz}^{-\frac{1}{2}} \text{ cm Hg}^{\frac{1}{2}}
\end{align*}
\]

It is of interest to compare these values with those predicted by the Helmholtz-Kirchhoff equation, although the latter is applicable to progressive waves. Using data from Tables of Thermodynamic and Transport Properties 1960, the experimental values are found to exceed the predictions by 20.4%, 18.0% and 20.1% respectively.
Gas mixtures

O₂ - H₂. Aviators' breathing oxygen was used throughout, and for this set of measurements small amounts of high purity commercial hydrogen were added. Over 80 different combinations of f/p and h (the molecular fraction of the impurity) were investigated. The values of h varied from 2 x 10⁻³ to 26 x 10⁻³ and the value of the frequency of maximum absorption, f₀, varied from 130 Hz to 1780 Hz. The dependence of f₀ on h was best expressed by the equation f₀ = -0.342 + 64.2h at 1 atm. The small negative term has no special significance and could be due to experimental error.

O₂ - He. Helium gas was obtained by evaporating liquid helium. From measurements over a range of frequencies for a single mixture with a molar fraction of He of 25.1 x 10⁻³ we obtained f₀ = 9 + 3.6h at 1 atm. As for the later mixtures, current data for pure oxygen have been included to obtain the first term. df₀/dh is about 0.8 times the value obtained by Parker (1961). It is possible that some air entered the helium in the present work, but this is unlikely to account for the above difference.

O₂ - CO₂. CO₂ was prepared in a Tucker generator with impurities not exceeding one part in 160,000. The results with about 60 different combinations of f/p and h included values of h in the same range as for H₂ and values of f₀ between 100 Hz and 800 Hz and gave f₀ = 9 + 45h at 1 atm. The value of df₀/dh shows good agreement with Henderson and Queen (1962) who obtained df₀/dh = 43.

O₂ - water vapour. The major obstacle to reliable work on O₂ - water vapour mixtures has been the difficulty of producing mixtures of accurately known composition. Water vapour is readily adsorbed on the surfaces with which it comes into contact. Reliability was obtained in the present work by a method involving measurements of the pressure exerted by the mixture. Further information is given in Harlow and Nolan (1967). The results with 50 different combinations of f/p and h gave f₀ = 9 + 162h + 144h² at 1 atm; the values of h varied from 0.7 x 10⁻³ to 2.3 x 10⁻³ and the values of f₀ varied from 200 Hz to 800 Hz.
Collision efficiency

If \( Z' \) is the average number of collisions for energy transfer between external and internal modes, we have for the first three mixtures
\[
Z_{O_2}' / Z_{H_2}' = 3300 \quad ; \quad Z_{O_2}' / Z_{He}' = 310 \quad ; \quad Z_{O_2}' / Z_{CO_2}' = 7260.
\]

Following Tuesday and Boudart (1955), the possible reactions occurring in the mixture of \( O_2 \) and water vapour may be written
\[
O_2^+ + O_2 \xrightarrow{k_{o_1}} O_2 + O_2; \quad O_2^+ + H_2O \xrightarrow{k_{o_2}} O_2 + H_2O; \quad O_2^+ + H_2O \xrightarrow{k_{o_3}} O_2 + H_2O^+; \quad H_2O^+ + H_2O \xrightarrow{k_{o_4}} H_2O + H_2O; \quad H_2O^+ + O_2 \xrightarrow{k_{o_5}} H_2O + O_2.
\]
The \( k \) coefficients are the rate constants of the reactions and an asterisk indicates excitation. The first reaction, involving \( O_2 \) only, is relatively slow, so that we have \( k_{10} \ll k_{20} \). We have \( k_{30} = 0.83 \ k_{03} \) and for the non-resonant exchange in the fifth reaction, \( k_{50} \ll k_{30} \). In the present work, \( h \) is negligible compared with 1 and we may arrive eventually at
\[
2n_f_o/p = k_{10} + (k_{20} + 0.83 \ k_{50})h + 0.83(k_{40} - k_{50})h^2.
\]
If we include the additional information provided by the work of Harris (1963) on mixtures of air and water vapour, we obtain the values
\[
k_{10} = 57; \quad k_{20} = 5 \times 10^5; \quad k_{30} = 1.6 \times 10^7; \quad k_{40} = 1.1 \times 10^9; \quad k_{50} = 5 \times 10^5.
\]
These show good agreement with the values obtained by Henderson and Herzfeld (1965), viz, 63; \( 5 \times 10^5; \quad 1.6 \times 10^7; \quad 1.0 \times 10^9; \quad 5 \times 10^5 \).

References


Vibrational Relaxation in Binary Mixtures between CO$_2$, N$_2$, CH$_4$, and H$_2$S.

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Germany

The direct transfer of vibrational energy between different modes in collisions of the kind that one mode is de-excited while the other mode is excited -- so-called "complex collisions" or Vib-Vib-processes -- is a dominant factor in the vibrational relaxation of gaseous mixtures, especially if a good resonance of the energy of the two quanta leaves only a small portion of the vibrational energy to be exchanged with translation.

For the most simple case, namely the binary mixture of two-level gases (i.e. if only one excited level is significantly occupied, see beneath) such a process transfers vibrational energy from molecule A to B and reverse. In this instance an exact theory is available $^1$ which has been confirmed already experimentally $^2$ $^3$: two relaxation processes are present; in a composition diagramm the corresponding relaxation rates conform a conic section which may, of course, degenerate into a pair of straight lines. From such a plot the transition probabilities P of the processes shown in the figure can be calculated, namely the normal de-excitation of both molecules in collisions with either A or B, and that of the Vib-Vib-process (P$_5$).

Frequently a good resonance of a two-level gas A does not exist to the lowest, but to a higher mode of the second, polyatomic, B. Then the Vib-Vib-process consists of at least two steps (cf. the figure beneath): Transfer to the higher mode and subsequent
Vibrational Relax. in Binary Mixtures between CO₂, N₂, CH₄, and H₂S

de-excitation to the lowest mode. Since the second step contains Vib-Vib-processes between several modes of one molecule, measurements in such mixtures furnish information about de-excitation mechanisms of higher modes not accessible from measurements in the pure gas B. The binary two-level theory ¹) can be applied to those mixtures, too, by taking an effective Vib-Vib-transition probability which may depend on composition because the second step may occur with either A or B as collision partner.

CH₄-H₂S mixtures: Among the mixtures studied in this paper, the system CH₄-H₂S can be regarded as binary two-level case, since the two lowest modes of CH₄ act as one level because of the high transition probability between them (cf. fig.5). Fig.1 shows the isothermal relaxation rates obtained from the measurements ⁴). The solid line is a best fit hyperbola (the upper portion cannot be detected experimentally because of lack of relaxation strength). From it the reciprocal transition probabilities shown in the left side of fig.5 have been calculated.

N₂-CO₂ mixtures: In the N₂-CO₂ system there is a close resonance to the asymmetric valence bond vibration ν₃ of CO₂ at 3380°K. Fig.2 shows as experimental result ⁵) two relaxation processes. The relaxation of the slower one (N₂ relaxation) is accelerated proportionally to the CO₂ content (100 s⁻¹atm⁻¹percent⁻¹) because of the high efficiency of the Vib-Vib-process, the faster one (CO₂) is affected only slightly by the different normal de-excitation probabilities of the collision partners N₂ and CO₂. If we assume the first step (N₂ → 3380°K) to be fast ⁶), from the slope of the slower process we obtain that 58 000 collisions with N₂ are necessary in the mean to de-excite the 3380°K-level to the lowest mode (960°K). From the lack of a quadratic dependence of 1/Τᵥ with composition we conclude a number between 40 000 and 130 000 collisions with CO₂ to be necessary for the same process. However, this reciprocal transition probabilities are still "over all" ones: Out of the various
paths we ascribe them to the one indicated in fig.5 at the right side with the bottleneck $3380^\circ K \rightarrow 2900^\circ K$.

**Fig. 2:** Sound absorption in $N_2$-$CO_2$ mixtures at $95^\circ C$.

**CH$_4$-CO$_2$ mixtures:** The CO$_2$ levels at approximately $1900^\circ K$ -- split due to Fermi resonance -- have a good resonance to the lowest modes.

**Fig. 3:** Isothermal relaxation rates in CH$_4$-CO$_2$ mixtures at $80^\circ C$.

**Fig. 4:** Relating molar heat capacities in CH$_4$-CO$_2$ mixtures at $80^\circ$
of CH₄. Fig.3 shows the isothermal relaxation rates obtained from the measurements. The best fit of the "modified two-level" theory (solid lines) yields a collision number of 2500 for the transfer CH₄ → 1900°K. The second step (1900°K → 960°K) is affected by two processes: Normal de-excitation in approximately 500 collisions with CH₄ and resonance production of two 960°K-states from one at 1900°K in 150 collisions with ground state CO₂. Fig.4 shows the relaxing molar heat capacities of the two processes gained from the acoustic relaxation strength. The fact that these do not follow the vibrational heat capacities of the single components (dashed lines) can be understood qualitatively by the theory, since the strong thermodynamic coupling of the excitational equilibria by the Vib-Vib-processes mixes the molar heat contributions of the single components to the full lines. However, a systematic surplus over the total vibrational heat capacity of the mixtures was found. There is no other way of explanation but to regard this surplus as a part of the rotational heat capacity which relaxes together with the vibrational one because of vibrational-rotational transitions of the kind that the vibration of CO₂ is de-excited while the rotation of CH₄ is excited. Such a picture is consistent with Cottrell's assumption of the fast rotation of the CH₄ molecule acting as the most non-adiabatic perturbation, not the translation. This would also explain the high efficiency of CH₄ for the normal de-excitation of CO₂.

Fig.5: Reciprocal collision probabilities per collision. The unchanged collision partner is denoted in parentheses. For the value of 11 in the CH₄-scheme see 4).

Acknowledgements: We wish to thank Mr. W. Auer for taking the measurements in the low frequency range of the N₂-CO₂ mixtures, and Mr. A. Paphitis for doing the measurements in the H₂S-CH₄ mixtures.

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4) H.-J. Bauer, A. Paphitis, R. Schotter, to be published
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Investigation of the Critical Region of Multicomponent Systems by the Ultrasonic Method.

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Doc. Professor of the Krupskaya Moscow Provincial Pedagogical Institute

It is known to investigate thermodynamic properties of matter and to establish laws of the thermodynamic order it is necessary to study the behaviour of principal physical and physical-chemical parameters of a large group of substances of various physical character. And so some complex investigation of liquids of many homological rows (alcoholic alcohols and aromatic hydrocarbon, monatomic alcohols, ethers of acetic and formic acids etc.) was carried out in our laboratory. The investigation was carried out in the wide range of temperatures beginning from the temperatures of crystallization of substances including their critical region. The investigation was carried out both at the line of saturation (under the conditions of dynamic equilibrium of the system liquid-vapour and at $p=\text{const.}$, $T=\text{const.}$, $V=\text{const.}$).

Inspite of the significance of this problem many thermodynamic and molecular-kinetic phenomena in this field have not been investigated yet.

Nowdays one of the main trends in the investigation of critical phenomena is studying of the principal thermodynamic parameters, characterizing the critical region. But in our opinion the investi-
Investigation of the Critical Region

gation of critical phenomena in multicomponent systems with the purpose of studying the physical nature of critical phenomena in individual substances is of not less importance.

In the coming year our laboratory continued its complex investigation of multicomponent systems at the line of saturation including the critical region.

The main aim was to investigate acoustical properties in the above mentioned systems: velocity and absorption of sound, volume viscosity. The optical method described in detail in our previous works was used to investigate the acoustical properties.

But at the same time some other physical-chemical parameters such as density, adiabatic compressibility, shear viscosity, thermal heat capacities were examined.

Some new results of the principal character were obtained. On the basis of these results it is possible to say definitely that from the point of view of thermodynamics the critical state of multicomponent systems has the same physical sense as the critical state in individual substances. The laws and rules obtained for individual substances are true for complex systems.

The gained material in the field of ultrasonic velocity measurement in the complex systems permits to make the necessary generalization and to establish simple analytical relations to connect the velocity of sound in multicomponent systems with other physical-chemical parameters.

It is natural that the simple relations connecting the velocity of ultrasonics in the components with the velocity of sound in the given mixture were the first to be examined. The following relation obtained in our laboratory several years ago was examined:

\[ C = \nu C_1 + (1-\nu) C_2 \]

Table 1 shows that this relation can be successfully applied to calculate the velocity of sound. It is natural that the divergency \( \nu \) from the experiment will be even less if we write down formula 1 in the following way:

\[ \frac{C_0}{C_{0=0.5}} = \nu \frac{C_0}{C_{0=0.5}} + (1-\nu) \frac{C_0}{C_{0=0.5}} \]

Then we used the principle of thermodynamic similarity to the case of multicomponent systems and established that the law of corresponding states is applied to the velocity of sound. This fact allows to calculate the velocity of sound in the mixture of any complexity both according to the value of the sound velocity in the mixture of another concentration and according to the value of it in one of the components.

Investigation of the critical region of mixture creates great possibilities for matter structure studying. Here we mean first of all the study of molecular effects in the critical region. Molecular acoustics states that one of the most sensitive parameters to the changes in the matter structure is volume viscosity. As an experimental fact of great principle importance we also should mention the discovery of maximum presence for volume viscosity in fully associated liquids such as methyl and ethyl alcohols. The same was established for binary mixtures one of the components of which is the above mentioned liquids. The effect itself in its value is far beyond the limits of the experiment error.

Qualitatively this result is explained well by supposition of fast decay of association complexes near to the critical point of ethyl and methyl alcohols.
Investigation of the Critical Region

<table>
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<th>№</th>
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<th>divergence (C - C exp) / C *100 (per centage)</th>
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<tr>
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</tr>
<tr>
<td>3.</td>
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<td>1.9</td>
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</tr>
<tr>
<td>9.</td>
<td>200</td>
<td>2.7</td>
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</table>

Mixture composition: A₁ - 20% C₂H₆ in the system (20% C₆H₆ in CH₃OH)
A₂ - 20% C₄H₁₀ in the system A₁
A₃ - 20% C₇H₁₆ in the system A₂
A₄ - 20% C₆H₁₂ in the system A₃
A₅ - 20% C₆H₁₄ in the system A₄

The ultrasonic investigations of the critical region of multicomponent systems also allowed to obtain rather valuable data for molecular physics. By means of the data of the sound velocity in the critical region it is possible to determine the critical temperature of mixtures of any complexity with great precision and moreover it is possible to obtain curves which are important both for physics and chemistry, for example, composition-critical temperature, pressure-composition etc.

The equipment designed in our laboratory permits to determine the critical pressure and the critical volume of a mixture simultaneously with the determination of the critical temperature of this mixture.

To determine the critical temperature the well-known experimental fact (passing of sound velocity through the minimum at the critical point) is used.

Table 2 shows the critical temperatures obtained by ultrasonic methods and for comparison - the critical temperatures obtained by other methods. At present the critical temperature is determined by this method in 44 systems of complex mixtures. The tables show that the values of critical temperatures obtained by various methods within experimental errors coincide.

"Thus by means of the curves composition-critical temperature" we can determine Tc of any mixture of the composition we are interested in.

If we take into consideration the fact that direct measurement methods are too bulky and take much time and ultrasonic methods allow to make the same measurement quickly it is possible to draw the conclusion that ultrasonic methods are the main methods for determining the most principle physical parameter.
<table>
<thead>
<tr>
<th>number of components</th>
<th>mixture composition, weight, %</th>
<th>Tcr (degrees)</th>
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<tr>
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<td></td>
<td>40% C₆H₆ in CH₃OH (B)</td>
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<tr>
<td></td>
<td>60% C₆H₆ in CH₃OH (C)</td>
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<td></td>
<td>80% C₆H₆ in CH₃OH (D)</td>
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<tr>
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<td>80% C₂H₅OH in the mixture A₆</td>
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Ultrasonic method of determining the density and the compressibility of liquids in function of pressure

Jerzy WEHR

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The well known application of ultrasonic measurements to the determination of compressibility of liquids [1], [2], [3], [4], is based on the relation:

\[ \beta_s = \frac{1}{\rho c^2} \] /1/

where \( \beta_s \) - adiabatic compressibility,
\( \rho \) - density,
\( c \) - propagation velocity of ultrasonic longitudinal waves.

The application of the above relation in the case of varying pressures has a great practical disadvantage - it requires namely the measurements of the density \( \rho \) in function of pressure, which are relatively difficult and expensive.

In principle the measurements of two quantities, \( \rho \) and \( c \), are not necessary to determine \( \beta_s \), the latter being connected with \( \rho \) by the equation of state. Knowing this equation we could, for known pressures and temperatures, eliminate \( \rho \) from the relation between \( \beta_s \) and \( c \). The equation of state being unknown for real liquids we shall use simple approximations and we shall prove, that the measurements of the velocity \( c \) are sufficient to determine both \( \beta_s \) and \( \rho \) in function of pressure, provided we know \( \rho \) at the initial pressure.
Deriving the formulas we shall take into consideration that it is much more convenient to carry out isothermic measurements than adiabatic ones. The isothermic compressibility $\beta_T$ is given by:

$$\beta_T = -\frac{1}{V} \frac{dV}{dp}$$

Putting $\beta_T = k \beta_s$, where $k = c_T / c_V$, we obtain:

$$\frac{dV}{V} = \frac{-k \cdot \beta_s}{\beta_s} dp$$

This equation cannot be integrated over a given interval of $p$ without knowing the functional relationship $\beta_s / p$. As known [5], compressibility modulus $K_T = 1 / \beta_T$ is practically linear in function of pressure in liquids at least till about 20-30 k阗. We shall assume $K_s$ linearly dependent on pressure in the pressure interval $p_1$, $p_2$, which also implies $k = \text{const.}$ in the same interval:

$$K_s = K_s + \alpha / p - p_1$$

where $\alpha$ - constant proportionality factor

Then, integrating /3/, we get:

$$V_2 - V_1 = \int_{p_1}^{p_2} \frac{k \cdot dp}{K_s + \alpha / p - p_1}$$

Substituting, after integration, $V_1 / V_2 = p_2 / p_1$ yields:

$$\ln \frac{p_2}{p_1} = K_s \frac{\alpha}{K_s} \ln \frac{K_s - p_2}{K_s - p_1}$$

Let us introduce new variables to abbreviate the notation:

$$\frac{c_1^2}{a} = a; \quad \frac{p_2}{p_1} = u; \quad \frac{K_s - p_2}{K_s - p_1} = z; \quad p_2 - p_1 = \Delta p$$

Eq. /6/ becomes then:

$$z = a \cdot \frac{\alpha}{K_s - p_1}$$

The density $\rho_1$ for the initial pressure $p_1$ being known, $K_s$ for the measured velocity $c_1$ is given by:

$$K_s = \rho_1 \cdot \frac{c_1^2}{\alpha}$$

On the basis of eq. /4/:
Ultrasonic determination of density and compressibility versus pressure

\[ \alpha = \frac{1}{z - 1} \frac{K_{sl}}{\Delta p} \] /9/

and we may rewrite eq. /7/ in the form:

\[ z = a \cdot \exp \left( \frac{\Delta p}{K_{sl}} \cdot \frac{\ln z}{z - 1} \right) \] /10/

putting

\[ \frac{\Delta p}{K_{sl}} \frac{\ln z}{z - 1} = x \] /11/

results in

\[ z = a \cdot \exp (x \cdot x) \] /12/

Eq. /12/ contains, besides of \( z \), an unknown quantity \( x \). We shall assume a simplified relation:

\[ \exp (x \cdot x) = \left( \frac{1}{1 - x} \right)^{\frac{1}{2}} \] /13/

which is fulfilled with errors < 2% for \( 1 \leq x \leq 1.5 \) and \( x \leq 0.05 \). This value of \( x \) allows for \( \Delta p \) as high as about 1000 atm/.

Then

\[ z = \frac{a}{1 - \frac{\Delta p}{K_{sl}} \frac{\ln z}{z - 1}} \] /14/

This kind of equation may be solved numerically by subsequent approximations:

\[ z_I = \frac{a}{1 - \frac{\Delta p}{K_{sl}} \frac{\ln z}{a - 1}} \] /15/

\[ z_{II} = \frac{a}{1 - \frac{\Delta p}{K_{sl}} \frac{\ln z_I}{z_I - 1}} \] /16/

\[ z_N = \frac{a}{1 - \frac{\Delta p}{K_{sl}} \frac{\ln z_{N-1}}{z_{N-1} - 1}} \] /17/

It may be noted, that the value of \( z_N \) lays always within the interval \( /a, z_I/ \).

Knowing the value of \( z \) we may calculate the compressibility \( \beta_{s2} \) as well as the density \( \rho_2 \), both corresponding to the velocity \( c_2 \).
Ultrasonic determination of density and compressibility versus pressure measured at pressure \( p_2 \):

\[
\rho_{s2} = \frac{\rho_{s1}}{z} = \frac{1}{\rho_1 c_1^2 z}
\]

\[
\rho_2 = \frac{\rho_1 z}{a} = \frac{\rho c_2^2 z}{c_2^2}
\]

The correction factor \( R \), resulting from the assumption /13/, by which the calculated value of \( z \) should be multiplied, is given by:

\[
R = \exp\left(\frac{c_2}{\rho c_2^2} / 1 - x\right)
\]

The value of \( x \) may be calculated from the following equation:

\[
x = 1 - \frac{a}{z} = 1 - \frac{1}{u}
\]

As known for liquids [6] \( x \) very seldom reaches 1.5 being usually \( \leq 1.0 \).

In the case of water at 30°C and at the atmospheric pressure, \( \Delta p = 1000 \) atm corresponds to \( x = 0.038 \) and to \( R < 1.005 \).

Comparison of the values of \( \rho \) directly measured in function of pressure [7] with those calculated according to the author's theory gives a very good agreement within 1%, which allows for the conclusion, that both the density and the adiabatic compressibility may be determined in function of pressure on the base of ultrasonic velocity measurements only, provided that the value of the liquid's density is known at the initial pressure.

References


Ultrasonic and Relaxational Spectroscopy of Fast Reactions
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Introduction
In the gas or liquid which is in an equilibrium of fast reactions, there occur absorption and dispersion of ultrasonic wave owing to the relaxations of molecular vibration, rotation or chemical reaction, and they give us a useful method for studying molecular structure and reaction kinetics. If there are many reactions, many ultrasonic absorption and dispersion appear, and the ultrasonic spectrum becomes complicated owing to the mutual interaction of the reactions. In this report, ultrasonic absorption and dispersion due to many reactions in gas and liquid are derived theoretically, and the physical meanings are examined. An automatic recording ultrasonic spectrometer is constructed and a method of analysis of ultrasonic data by a digital computer is discussed.

Complex Velocity of Sound
Since we have no space to show the general expressions of $n$ reactions, we show an example of two reactions. When there are two reactions
\begin{align*}
a_1A + b_1B + \cdots & \rightleftharpoons q_1Q + r_1R + \cdots \\
a_2A + b_2B + \cdots & \rightleftharpoons q_2Q + r_2R + \cdots
\end{align*}
in gas, the complex velocity of sound $\nabla$ is given by
\begin{equation}
\nabla^2 = \frac{P}{f} \frac{C_p + \left( C_p' \right)_1 + \left( C_p' \right)_2 + \left( C_p' \right)_3}{C_v + \left( C_v' \right)_1 + \left( C_v' \right)_2 + \left( C_v' \right)_3} , \quad C_p = C_v + \pi R ,
\end{equation}
Ultrasonic and Relaxational Spectroscopy

\[
(C_p^\gamma)_l = \left[ \frac{E_s^2}{RT^2} - \varepsilon, (2 \frac{E_s}{T} + \varepsilon, \frac{C_v}{\pi}) \right] / \chi_{1,1} (1 + j \omega \tau) ,
\]

\[
(C_p^\gamma)_a = \left[ \frac{E_s^2}{RT^2} - \varepsilon, (2 \frac{E_s}{T} + \varepsilon, \frac{C_v}{\pi}) \right] / \chi_{2,2} (1 + j \omega \tau) ,
\]

\[
(C_p^\gamma)_{la} = - \left[ \frac{E_s^2}{RT^2} + \xi, \frac{E_s}{\pi} \right] + \{ \frac{E_s^2}{RT^2} + \xi, \frac{E_s}{\pi} \} \chi_{12} (1 + j \omega \tau) / \chi_{11} (1 + j \omega \tau) ,
\]

\[
(C_p^\gamma)_l = \frac{E_s^2}{RT^2} / \chi_{11} (1 + j \omega \tau) , \quad (C_p^\gamma)_a = \frac{E_s^2}{RT^2} / \chi_{22} (1 + j \omega \tau) ,
\]

When there are two reactions in liquid, the complex velocity of sound \( \nabla \) is given by

\[
\nabla^2 = \frac{1}{\rho \beta_r} \left( C_p + (C_p^\gamma)_l + (C_p^\gamma)_a + (C_p^\gamma)_{la} \right) - \frac{1}{\rho \beta_r} \left( C_p + (C_p^\gamma)_l + (C_p^\gamma)_a + (C_p^\gamma)_{la} \right) , \quad C_p = C_v + \frac{1}{\rho \beta_r} \frac{\nabla^2}{\rho \beta_r} ,
\]

\[
(C_p^\gamma)_l = \frac{E_s^2}{RT^2} (\xi, \frac{E_s}{\pi} - \xi, \frac{E_s}{\pi} ) - \{ \frac{E_s^2}{RT^2} - \xi, \frac{E_s}{\pi} \} \chi_{12} (1 + j \omega \tau) ,
\]

\[
(C_p^\gamma)_a = \frac{E_s^2}{RT^2} / \chi_{12} (1 + j \omega \tau) , \quad (C_v^\gamma)_l = \frac{E_s^2}{RT^2} / \chi_{12} (1 + j \omega \tau) ,
\]

where \( \rho \) is the pressure, \( \rho \) the density, \( \nu \) the volume, \( \tau \) the total number of moles, \( \beta_r \) the gas constant, \( T \) the absolute temperature, \( \ell \) the expansion coefficient, \( \beta_r \) the compressibility at constant temperature, \( E_m \) the reaction heat at constant volume of the \( m \)-th reaction, \( v_m \) the reaction rate of the \( m \)-th reaction, \( \tau_m \) the relaxation time of the \( m \)-th reaction, \( (r_m) \) the reaction rate of the equilibrium.

\[
\xi_m = (a_m + b_m + \cdots ) - (g_m + r_m + \cdots ) ,
\]

--- J-26 ---
\[ x_{lm} = \left( \frac{a_l a_m}{n_A} + \frac{b_l b_m}{n_B} + \ldots \right) + \left( \frac{g_l g_m}{n_{\alpha}} + \frac{\gamma_l \gamma_m}{n_{\beta}} \right), \]
\[ \frac{1}{\tau_m} = \left( \tau_m \right)_{o v} x_{mm}. \]

From the above equations, it is seen that the heat capacity at constant pressure and at constant volume are given by the sum of \( C_p, \)
\( C_v, \) the heat capacity as the simple mixture, \((C_{p}^r)\), \((C_{v}^r)\), the heat capacity due to the first reaction, \((C_{p}^{r_1})\), \((C_{v}^{r_1})\) the heat capacity due to the second reaction, and \((C_{p}^{r_2})\), \((C_{v}^{r_2})\), the heat capacity due to the mutual interaction of the two reactions.

**Velocity and Absorption Coefficient of Sound**

Velocity \( \nabla \) and absorption coefficient \( \alpha \) of sound are derived from the complex velocity of sound. \( \lambda \) is the wavelength.

\[ \mu = \alpha \lambda = 2\pi \left[ \left\{ \frac{1 + (\tan \varphi)^2}{1 - (\tan \varphi)^2} \right\}^{\frac{1}{2}} - (\tan \varphi)^{-1} \right], \]
\[ \nabla^2 = \frac{\left(1 + (\frac{\mu}{2\pi})^2\right)}{1 - (\frac{\mu}{2\pi})^2} \frac{Re(\nabla^2)}{Re(\nabla^2)}, \quad tan \varphi = \frac{Im(\nabla^2)}{Re(\nabla^2)}. \]

If the phase angle is small, we have \( \nabla^2 = Re(\nabla^2), \quad \mu = \pi tan \varphi. \)

**Automatic Recording Ultrasonic Spectrometer**

In order to measure ultrasonic spectrum, an automatic recording ultrasonic spectrometer is designed and constructed. The block diagram of the ultrasonic spectrometer is shown in Fig. 1. With this spectrometer, ultrasonic absorption is measured by the pulse echo method at 24 frequencies from 100 kc to 310 Mc/sec, and ultrasonic velocity is measured by the sing-around method at 8 frequencies from 1 Mc to 23 Mc/sec. Once the measurement is started, all measurements are proceeded automatically by a method of sequence control. The measured results on absorption are recorded by a X-Y recorder, punched in tapes and typed with the results on velocity. If we put the tapes into a digital computer, the ultrasonic spectrum and the parameters are calculated, and the results are punched in tapes, typed and drawn in figures through a digital plotter. The programings of the digital computer for analysis of ultrasonic data of any number of relaxations are also discussed.
Fig. 1 Block diagram for automatic recording ultrasonic spectrometer
Measurement of Ultrasonic Absorption and Velocity in Liquids by Resonance Reverberation Method.

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Introduction

The reverberation method for measuring sound absorption in liquids has been used by several authors.\(^1\) Results by this method, however, show a considerable scatter among authors, especially below 50 kHz. The aim of this study is to present an improved technique for the method, in which the effect of container is eliminated and measurement of velocity as well as absorption to so low as 10 kHz can be made.\(^7\) Results for toluene, butanol, and aqueous solutions of various sulfates will be presented.

Experimental

The equation for the decay rate of reverberation \(D\), in a spherical container after the excitation has been stopped is

\[
D = \frac{1}{t} \ln \frac{a}{a_0} = \left[ -\frac{k}{\alpha} \ln (1 - \beta) + \alpha \right] c,
\]

where \(c\) is the sound velocity of liquid, \(\alpha\) the absorption coefficient of liquid, \(k\) the constant, and \(a\) the radius of the container. The surface absorption coefficient \(\beta\) depends in general on following factors; (1) shape, wall thickness, and material of the container, (2) acoustic impedance of liquid, (3) resonance mode of vibration of the whole system.

When a reference liquid is used which has a similar acoustic impedance to the sample liquid and the decay rate is compared at the same resonance mode (not at the same frequency), \(\beta\) is constant and hence

\[
\alpha = \alpha_i + \left( \frac{D}{c} - D_i/c_i \right),
\]
Ultrasonic Absorption Measurement by Reverberation Method

where suffix 1 refers to the reference liquid. If the reference liquid is expected to exhibit no relaxation at covered frequencies and hence \( \alpha_1 \) can be extrapolated from high frequency absorption, we can obtain \( \alpha \) from eq.(2).

The value of \( \text{ka} (k=2\pi/\lambda) \) at the resonance of liquid in the rigid spherical container is characterized by three integers. Accordingly, at the same resonance mode, the ratio of resonant frequencies is

\[
\frac{f}{f_1} = \frac{c}{c_1}.
\]

This equation enables us to obtain \( c \) by this method.

A block diagram of the apparatus is illustrated in Fig.1. The variable frequency oscillator was designed to have a good frequency stability. A pair of barium titanate transducers having a fundamental resonance of 1 MHz were used for sending and receiving the acoustic energy, respectively. The input electrical power was so low that no cavitation was observed. The logarithmic amplifier had

\[\left(\frac{\alpha}{\text{k}^2}\right)_B \quad \left(10^{-17} \text{S/cm}^{-1}\right)\]

\[\text{FREQUENCY (kc/sec)} \quad 10 \quad 100 \quad 1000\]

\[\text{35°} \quad 25° \quad 20° \quad 14°\]

\[\text{Fig.2. Absorption coefficient of toluene. Arrows indicate } f_1.\]

\[\left(\frac{\alpha}{\text{k}^2}\right)_B \quad \left(10^{-17} \text{S/cm}^{-1}\right)\]

\[\text{FREQUENCY (kc/sec)} \quad 10 \quad 100 \quad 1000\]

\[\text{32} \quad 33 \quad 34 \quad 35\]

\[\nu x 1400 \text{ cm}^{-1} \quad \nu x 2980 \text{ cm}^{-1} \quad \nu x 5140 \text{ cm}^{-1}\]

\[n=1 \quad n=2 \quad n=3\]

\[\text{Fig.3. Comparison of } (\alpha_x)_{\max} \text{ of toluene with theory,}\]

\[(\alpha_x)_{\max} C_P^{-1} = \frac{n \pi}{2 R} \left( N_{ph} k \nu \right) \exp \left( \frac{N_{ph} k \nu}{RT} \right)\]
a sufficiently short time constant and a logarithmic characteristic over a range of 60 db. The time between two levels of the reverberation was measured with an electronic counter to the accuracy of 0.1 db/sec.

Spherical Pyrex glass flasks with the volume of 2 to 10 litres were used as containers. The container was supported with piano wires and placed in a vacuum chamber. The chamber was set in an air thermostat and the temperature of the liquid was measured to 0.1 degree before and after the acoustic measurement.

The resonance frequency was detected to 0.1 Hz from the sharp minimum of decay rate. The same mode for sample and reference liquids was ascertained from the condition of eq.(3).

Toluene

Results for toluene are drawn in Fig.2. Xylene was used as the reference. The curve at each temperature is fitted by the single relaxation process,

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_r)^2} + B \quad (4)$$

The relaxation time $\tau = 1/2\pi f_r$ decreases with increasing temperature.
with the activation energy of 4.4 kcal/mole. The relaxation strength A increases with increasing temperature. Experiments for toluene-xylene mixtures revealed that A decreases rapidly with increasing xylene content, but \( f_r \) remains almost unchanged. Benzene shows no relaxation around 20 kHz and has \( \alpha/f^2 \) value equal to that at megacycle range.

Toluene exhibits another acoustic relaxation around 6 GHz, and one or two dielectric relaxations above 10 GHz. Origins of these relaxations are not fully described at present. The value of \( (\alpha_x)_{\text{max}} \) of low frequency acoustic relaxation is smaller than published in literatures and may be interpreted in terms of intramolecular vibrational degrees of freedom in methyl group.

Butanol

Results for iso-butanol are drawn in Fig. 4. Acetone was employed as the reference. The relaxation strength slightly decreases with increasing temperature. The activation energy of relaxation time is 9.4 kcal/mole. n-Butanol shows a similar relaxation with the activation energy of 8.7 kcal/mole. The relaxation may be possibly assigned to molecular association but further work is necessary to reach the conclusion.

Aqueous Solutions of Sulfates

Fig. 5 represents the absorption of MgSO\(_4\) solutions obtained with water as the reference. Data by Wilson and Leonard shown in Fig. 5 by the broken line (0.02 mol/l) suggests possibility of another relaxation below 50 kHz but this is not observed in the present data. The dispersion of sound velocity between 3 MHz and 28 kHz is drawn in Fig. 6, observed by the sing-around method and the present one, respectively. The difference is proportional to concentration and 4 cm/s at 0.02 mol/l, which is consistent with the calculated value from \( (\alpha_x)_{\text{max}} \) in Fig. 5.

Results for various surfactes were obtained from 10 to 300 kHz. The values agree well with those by Kurtze and Tamm above 50 kHz.

References
Kinetic Studies of Intramolecular Hydrogen Bonding in Methyl Salicylate and Salicylaldehyde by means of Ultrasonic Absorption Measurement

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Introduction

Relaxational techniques have extensively been applied to kinetic studies of rapid chemical reaction,\textsuperscript{1,2} such as intermolecular hydrogen bonding, hydrolysis and protolysis of electrolyte, and rotational isomerism. Only a limited number of investigations have been made on kinetics of intramolecular hydrogen bonding by means of temperature jump method\textsuperscript{3}, although the role of the hydrogen bond in biological systems has been the source of considerable speculation and numerous experimental studies.\textsuperscript{4}

It has been well known by the ordinary spectroscopic methods that in methyl salicylate or salicylaldehyde\textsuperscript{5} a phenolic hydroxyl group forms a strong intramolecular hydrogen bond with an oxygen of adjacent carboxyl or carbonyl group, but its kinetic study has not yet been done. The purpose of the present investigation is to decide the mechanisms of sound absorption in methyl salicylate and salicylaldehyde and to calculate the kinetic values for the reaction associated with those.

Experimental

The measurements of sound absorption were made over the frequency
Ultrasonic Absorptions in Methyl Salicylate and Salicylaldehyde

range 2.5 to 95 Mc at various temperatures, 15 to 40°C by means of pulse method. The velocity of sound was measured at 3 Mc by an ultrasonic interferometer. Chemicals were all the guaranteed reagents and were used throughout this study without further purification.

Results and discussion

The plots of data are presented in Fig. 1 along with their corresponding theoretical curves represented by the following equation for single relaxation:

\[ \frac{\alpha'}{f^2} = \frac{\alpha}{f^2} - B = \frac{A}{1 + \left(\frac{f}{f_{\text{max}}}\right)^2}, \]  

where \( \alpha \) is an absorption coefficient of sound, \( \alpha' \) is the relaxational absorption coefficient, \( A \) and \( B \) are the relaxational absorption and classical absorption, respectively, \( f \) is the frequency of sound, \( f_{\text{max}} \) is the frequency at the maximum of the absorption per wavelength \( \alpha' \lambda \). The relaxational absorption can be seen in the lower frequencies than 8 Mc in methyl salicylate and salicylaldehyde and at 8.5 Mc in 2.17 M dioxane solution of salicylic acid. While, the spectra in methyl benzoate and 1.66 M dioxane solution of benzoic acid do not show such an absorption although a very weak relaxational absorption can be seen at around 40 Mc in the latter solution.

The reaction heat capacities at constant pressure and volume, \( C_p^r \) and \( C_v^r \), calculated by Tabuchi’s equations using the data of the absorption and others. The value for \( C_p^r \) is equal to that for \( C_v^r \) so that the volume change resulting from the reaction is absent. As the reaction is not accompanied with the volume change the following ones may be considered to occur in these compounds.
Ultrasonic Absorptions in Methyl Salicylate and Salicylaldehyde

1. Intramolecular hydrogen bonding

\[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{O}} \\
\end{align*} \]

2. Intermolecular hydrogen bonding

\[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{O}} \\
\text{or} & \\
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{O}} \\
\end{align*} \]

3. Isomerization of rotational isomers

\[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\end{align*} \]

Table I. Sound absorption and types of reaction

<table>
<thead>
<tr>
<th>Name of sample</th>
<th>Chemical structure</th>
<th>Absorption in lower freqs. than 8 Mc</th>
<th>Reaction type</th>
</tr>
</thead>
</table>
| methyl salicylate | \[ \begin{align*}
\text{O} & \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} & \quad \text{\text{H}} \\
\end{align*} \] | X | X | - | X |
| salicylaldehyde | \[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\end{align*} \] | X | X | - |
| salicylic acid | \[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\end{align*} \] | - | X | X | - |
| methyl benzoate | \[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\end{align*} \] | - | - | - | X |
| benzoic acid | \[ \begin{align*}
\text{O} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\text{\text{O}} & \quad \text{\text{C}} \quad \text{\text{H}} \\
\end{align*} \] | - | - | X | - |

Applicable boxes were checked with X.

The reaction ① is alone satisfied with the experimental results. Therefore the absorptions in methyl salicylate and salicylaldehyde are probably associated with the intramolecular hydrogen bonding.

For the intramolecular hydrogen bonding which is the unimolecular reaction, Tabuchi's equations are represented by the following equation:

\[ C_v^p = \left( \frac{E^2}{RT^2} \right) \delta (1-\delta) \]

\[ (2) \]
Ultrasonic Absorptions in Methyl Salicylate and Salicylaldehyde

where $\delta$ is the mole fraction of reactant and $E$ is the heat of reaction at constant volume. The integrated van't Hoff isochore is

$$\ln K_1 - \ln K_2 = (E/R)(T_1^{-1} - T_f^{-1}),$$ (3)

where $K$ is the equilibrium constant which is given by

$$K = (1-\delta)/\delta.$$ (4)

The forward and backward rate constants of this reaction, $k_F$ and $k_B$, are represented by the following equation:

$$\tau^{-1} = k_B(1+K) = k_F(1+1/K),$$ (5)

where $\tau$ is the relaxation time. The kinetic values are calculated, by the temperature dependence of sound absorption using Eqs. (2)-(5).

The forward and backward rate constants at 30°C are $1.2 \times 10^6$ and $3.1 \times 10^7$ sec$^{-1}$ for methyl salicylate and $3.8 \times 10^5$ and $2.4 \times 10^7$ sec$^{-1}$ for salicylaldehyde, respectively. The heats of the hydrogen bonding are 2.5 and 3.1 kcal/mole for methyl salicylate and salicylaldehyde, respectively. The backward heats of activation are 5.8 and 8.8 kcal/mole for methyl salicylate and salicylaldehyde, respectively.

References

Hyperakustische Eigenschaften der Azeton-Chloroform-Lösungen

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In dieser Arbeit wurden die Geschwindigkeit und die Absorption des Hyperschalles gemessen mit Hilfe der Feinstruktur der Linie der Rayleigh-Lichtstreuung in den Lösungen Azeton-Chloroform.

Diese Lösungen sind dadurch gekennzeichnet, daß beim Lösen die Azeton- und die Chloroformmoleküle die intermolekularen Wasserstoffbindungen bilden \((\text{CH}_3)_2\text{CO} \ldots \text{H-CCl}_3\) , obwohl die reinen Komponenten die unassoziierten Flüssigkeiten sind.

Die Spektren der Feinstruktur der Rayleigh-Linie wurden mit Hilfe einer Apparatur aufgenommen, in welcher ein He-Ne-Laser (mit der Leistung von 20 mW), ein Perot-Fabry Interferometer mit einem Trennungsring von 10 mm und ein Objektiv mit \(F=800\) mm benutzt wurden.

Die Geschwindigkeit des Hyperschalles ist bis auf 0,5% präzise bestimmmt, die Absorption bis auf 20%.

Die Abhängigkeit der Schallgeschwindigkeit von der Konzentration ist in der Abb.1 graphisch wiedergegeben. Mit " o " sind die Geschwindigkeiten des Ultraschalles bezeichnet, die bei der Frequenz von 24 MHz gemessen wurden, mit " x " – die Resultate für den Hyperschall bei der Frequenz \(\sim 3200\) MHz. Die letzteren wurden von uns
aus der Lage der Mandelstam-Brillouin-Komponente im Rayleigh-Triplet bestimmt. Die Geschwindigkeit des Ultraschalles hängt monoton von der Konzentration ab, wobei im Bereich 1,0–0,45 Molteile des Azetons die Ultra- und die Hyperschallgeschwindigkeiten zusammenfallen. Bei kleineren Azetongehalten wird eine positive Dispersion beobachtet, die mit der zunehmenden Chloroformkonzentration größer wird. Im reinen Chloroform beträgt die Dispersion der Schallgeschwindigkeit etwa 5%.

Die Konzentrationsabhängigkeit der Ultraschallgeschwindigkeit ist also monoton, und die entsprechende Kurve für den Hyperschall besitzt ein scharfes Minimum im Bereich der großen Chloroformkonzentrationen.

Die Absorption des Ultraschalles in Azeton-Chloroform-Gemischen wurde im Frequenzbereich von 40 bis 900 MHz bestimmt. Wie aus der Abb. 2 ersichtlich ist, fällt der Absorptionskoeffizient des Ultra-
schalles mit zunehmendem Azetongehalt von $475.10^{-17} \text{sek}^2 \text{cm}^{-1}$ bis zu $30.10^{-17} \text{sek}^2 \text{cm}^{-1}$ monoton ab (Kurve 1). Im Bereich der großen Chloroformkonzentrationen (1,0–0,9 Molteile) tritt für die Frequenzen 40 – 900 MHz eine Dispersion der Ultraschallabsorption auf.

Die Kurve 2 wiedergibt die Konzentrationsabhängigkeit des Koeffizienten der Hyperschallabsorption bei der Frequenz von 3200 MHz. Von reinem Azeton an und bis zu 0,2–0,3 Molteile Azetons fallen die Kurven 1 und 2 zusammen, d.h. für diese Konzentrationen bleibt die Abhängigkeit des Absorptionskoeffizienten quadratisch bis zu den Hyperschallfrequenzen.

Bei den großen Chloroformkonzentrationen ist der Absorptionskoeffizient des Hyperschalles viel kleiner als der des Ultraschalles. Beim Chloroformgehalt von 0,8 Molteilen weist die Kurve 2 ein Maximum auf.

In den Azeton-Chloroform Lösungen ist die Schallabsorption durch zwei Ursachen bedingt: Schwingungsrelaxation und Prozesse, die mit der Komplexbildung verbunden sind.

Die Schwingungsrelaxationszeit in reinem Chloroform ist $\tau \sim 10^{-10} \text{sek }/1/$, in reinem Azeton sie ist $\tau \sim 10^{-12} \text{sek }/2/$. Das Chloroform absorbiert den Ultraschall stark, das Azeton dagegen schwach.

Wie aus unserem Experiment hervorgeht, wenn man zum starkabsorbierenden Chloroform das schwachabsorbierende Azeton hinzufügt, fällt die Ultraschallabsorption anfangs stark ab, bei der weiteren Zugabe des Azetons ändert sich die Absorption nur wenig. Die Zugabe des Azetons verkleinert die Zeit der Schwingungsrelaxation der Lösung, und das Relaxationsbereich verschiebt sich in Richtung größerer Frequenzen.

Das Maximum der Konzentrationsabhängigkeit des Absorptionskoeffizienten und das Minimum für die Abhängigkeit der Hyperschall-
Hypersakustische Eigenschaften der Azeton-Chloroform Lösungen

geschwindigkeit bei 0,2 Molteilen Azetons und bei den Frequenzen
3.10^9 Hz sind wahrscheinlich dadurch zu erklären, daß bei diesen
Frequenzen ein anderes Relaxationsmechanismus eintritt, wo die
Bildung und Zerstörung der Komplexe von der Art (CH₃)₂CO...HCCl₃ und
(CH₃)₂CO...2HCCl₃ zustande kommen.

Diese Annahme wird durch die Resultate von M.I.Schachparonow
und W.A.Wakalow /3/ bestätigt, die bei der Untersuchung der dielek-
trischen Eigenschaften dieser Lösungen gefunden haben, daß die Le-
benszeiten der erwähnten Komplexe sehr klein sind, von der Ordnung
10⁻¹¹ - 10⁻¹² sek. In diesem Fall muß die Frequenz der Struktur-
relaxation 10¹⁰ - 10¹¹ Hz betragen.

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Ultrasonic Relaxation in Organic Liquids and Solutions within Frequency Range of 20-1500 Mc/sec

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Introduction

Theoretical ideas and experimental facts show that ultrasonic relaxation in liquids appear in a very wide frequency range. It is possible however to give a complete idea of the mechanism of the effects of relaxation in some of Kneser liquids and aqueous solutions of electrolytes even now. Ultra high frequency measurements which are discussed in this paper were carried out by ultrasonic pulse method at nearly the same frequencies which could so far be obtained only with the help of optical hypersonic units.

Methods Used

The absorption measurements have been made by ordinary pulse method at selected frequencies between 20 and 300 Mc/s. For higher frequencies the equipment was designed where sound waves were generated by the surface excitation of X-cut quartz crystal rods in the electric field of a resonant cavity and similarly detected by the other. Liquids under investigation were placed between the crystal rods, ultrasonic path length in them at UHF not exceeding 50 microns. Crystal rods were connected with optical system measuring the acoustic path length. The amplitude of the acoustic signal in our method
was proportional to the number of interference bands, transformed by photomultiplier into electric signals for precise registration.

**Organic Liquids**

The results of the experiments \(\alpha/f^2 \cdot 10^{-17} \text{cm}^{-1} \text{s}^2\) in several organic liquids at temperature 20°C are given in table 1.

**Table 1**

<table>
<thead>
<tr>
<th>Liquid</th>
<th>500</th>
<th>650</th>
<th>850</th>
<th>1000</th>
<th>1200</th>
<th>1350</th>
<th>1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CS}_2) (t=25°C)</td>
<td>135</td>
<td>84</td>
<td>56</td>
<td>41.5</td>
<td>27.5</td>
<td>24.3</td>
<td>19.6</td>
</tr>
<tr>
<td>(\text{C}_4\text{H}_4\text{S})</td>
<td>409</td>
<td>285</td>
<td>182</td>
<td>127</td>
<td>100</td>
<td>80</td>
<td>65</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_6)</td>
<td>588</td>
<td>465</td>
<td>350</td>
<td>260</td>
<td>203</td>
<td>163</td>
<td>145</td>
</tr>
<tr>
<td>(\text{C}_6\text{H}_6\text{CH}_3)</td>
<td>82</td>
<td>82</td>
<td>80</td>
<td>78.4</td>
<td>75</td>
<td>75</td>
<td>73</td>
</tr>
<tr>
<td>(\text{CCL}_4)</td>
<td>506</td>
<td>497</td>
<td>450</td>
<td>390</td>
<td>339</td>
<td>315</td>
<td>290</td>
</tr>
<tr>
<td>(\text{CHCl}_3)</td>
<td>370</td>
<td>323</td>
<td>270</td>
<td>235</td>
<td>191</td>
<td>175</td>
<td>146</td>
</tr>
<tr>
<td>(\text{CH}_2\text{Cl}_2) (t=25°C)</td>
<td>168</td>
<td>107</td>
<td>78</td>
<td>56</td>
<td>47.6</td>
<td>40.2</td>
<td>40</td>
</tr>
</tbody>
</table>

![Graph 1](image1.png)  
![Graph 2](image2.png)

Fig. 1 Sound absorption of \(\text{CS}_2\) and \(\text{C}_4\text{H}_4\text{S}\)

Fig. 2 Sound absorption of \(\text{CH}_2\text{Cl}_2\)

Absorption in most of these liquids is due to total vibrational specific heat \(/1-5/\). The results of our experiments illustrate these relaxation effects up to frequencies of 1500 Mc/s. The analysis of the acoustic data for \(\text{C}_4\text{H}_4\text{S}\) (Fig. 1) shows that the relaxation of the
Ultrasonic Relaxation in Organic Liquids

total vibrational specific heat with a single relaxation time is as true as in the case with CS₂ /2/. The absorption in CH₂Cl₂ (Fig.2) has a complex character, which does not correspond to a single relaxation time. This confirms the point of view given in previous investigations /4-5/.

Electrolyte Solutions

Though there is a great number of investigations concerning the acoustic properties of aqueous solutions of electrolytes there are very few studies dealing with the UHF relaxation /7,8/. In this part we give the results of the absorption measurements in aqueous solutions of CdI₂, CdCl₂ and sulphates Na, NH₄, Mg, Mn, Cu within the frequency range of 20-1000 Mc/s (Table 2, Fig.3,4).

Table 2

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>CdI₂</th>
<th>CdCl₂</th>
<th>MgSO₄</th>
<th>MnSO₄</th>
<th>CuSO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>t °C</td>
<td>20</td>
<td>20</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>C mole/litre</td>
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<td>1.0</td>
<td>0.5</td>
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<td>0.1</td>
</tr>
<tr>
<td>f Mc/s</td>
<td>62</td>
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</tr>
<tr>
<td>Γ x 10¹⁰s</td>
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<td>28</td>
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</table>

It is known that cadmium halides exist in solutions very largely in the form of complexes. In this case the excess absorption is due to a disturbance of the equilibrium between the particles associated in complexes and free ions by a passing sound wave. The formation of complexes brings about the reduction in the total number of ions in the solution and thus lowers the internal pressure which in its turn causes increase in absorption. This explains a significant absorption in CdI₂ and CdCl₂.

The results of the sound absorption in sulphates are discussed from the point of view of the theory by M.A. Leontovich /9/ according to which the ionic atmosphere relaxation is possible at high frequencies. As follows from the theory the absorption rises with the in-
Ultrasonic Relaxation in Organic Liquids

Fig. 3 Sound absorption of aqueous solutions CdI₂

Fig. 4 Relaxation curves of sulphates Na, NH₄, Mg, Mn, Cu increase in concentration, the relaxation time lowers and for 0.1 mole/litre solutions is \(4 \times 10^{-9}\) s, for 0.5 mole/litre - \(2.5 \times 10^{-10}\) s, for 1.0 mole/litre - \(10^{-10}\) s. These theoretical conclusions are proved by experimental data.

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Acoustic Dispersion and its Mechanism in Benzene, Pyridine, Chloroform and Some Other Liquids in Frequency Range 10 - 5000 Mc/s

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Moscow State University

The aim of the present paper is to study the mechanism of acoustic dispersion in liquid benzene, carbon disulphide, pyredine, chloroform, thiophene, methylene bromide and methylene chloride on the basis of ultra and hyperacoustic measurements.

Sound absorption and velocity in the range from 10 to 1000 Mc/sec were measured by the pulse method of variable distance. At higher frequencies of 10 Gc/sec the measurements were carried out by an optical method with due allowance for the data on thin structure of the line of Rayleigh's light scattering with helium - neon lazer.

To a first approximation the results of our experiment may be described by the following formula:

\[ \frac{\alpha}{\tau^2} = B + \frac{A}{1 + \omega^2 \tau^2} \]

where \( \alpha \) means amplitude coefficient of sound absorption; \( \omega = 2\pi f \) is circular frequency; \( A \) and \( B \) are relaxation parameters; \( \tau' = (2\pi f_0) \) is relaxation time.

The experimental values of \( A, B, \tau \) and values of \( C_p \) which means specific heat at constant pressure \( C_v \) which means specific heat at constant volume and \( C' \) which means full vibrational specific heat
calculated according to Einstein formula, on the basis of the data on oscilatory spectrum C₆H₆, CS₂, C₅H₅N, CHCl₃, C₄H₆S, CH₂Br₂, CH₂Cl₂ are recorded in the Table.

Formula (1) apart from parameter \( \tau \) contains parameter \( B \) which is selected empirically. Therefore the fact that the experimental data are described by equation (1) does not mean that only one acoustic relaxation time is present in the investigated liquids. In this connection it is advisable to use other methods in the description of experimental data in the field of acoustic dispersion. The method suggested by Knese is one used for the purpose.

According to Knese:

\[
\left( \frac{\alpha'}{\pi} \cdot \frac{V_0^2}{V} \right)^2 + \left[ \frac{V_o^2}{V} - \frac{V_o^2 + V_\infty^2}{2V_\infty} \right]^2 = \left[ \frac{V_\infty^2 - V_o^2}{2V_\infty^2} \right]^2 \tag{2}
\]

Here means excessive absorption; \( \lambda \) means sound wave length; \( V_0, V \) and \( V_\infty \) are sound velocity with \( \omega \to 0 \), \( \omega = 2\pi f \) and \( \omega \to \infty \), respectively.

The values of \( V_0 \) and \( V_\infty \) are given in the Table.

If the value \( \left( \frac{\alpha'}{\pi} \frac{V_0^2}{V} \right) \) is plotted on the ordinate axis and the value \( \left( \frac{V_o}{V} \right)^2 \) is plotted on the abscissa, then with one relaxation time the experimental points on the form a half circle with the centre on the abscissa. In case of several relaxation times, the diagram acquires more complicated form.

The graph plotted in compliance with experimental data obtained for CS₂ is a half circle with the centre on the abscissa. This confirms our assumption that acoustic dispersion in CS₂ may be described
by the equation with one relaxation time (Fig.1):
\[
\left( \frac{V_0}{V} \right)^2 - \frac{1}{\pi} \left( \frac{\alpha \lambda}{V} \right) = \left( \frac{V_0}{V} \right)^2 \omega^{-\infty} + \left[ \left( \frac{V_0}{V} \right)^2 \left( \frac{V_0}{V} \omega^{-\infty} \right) \right]^{-1}
\]
(3)

In case of \( C_6H_6 \), experimental points form an inclined curve and may be described by the formula (Fig.2):
\[
\left( \frac{V_0}{V} \right)^2 - \frac{1}{\pi} \left( \frac{\alpha \lambda}{V} \right) = \left( \frac{V_0}{V} \right)^2 \omega^{-\infty} + \left[ \left( \frac{V_0}{V} \omega^{-\infty} \right) \right]^{-\beta}
\]
(4)

With \( C_5H_5N, CHCl_3, C_4H_4S, CH_2Br_2, \) the experimental points form a half circle with the centre below the abscissa. The shape of this half circle is identical to the diagrams by Cole and Cole (Fig.3). The graphs of such kind are indicative of the presence of the distribution of relaxation times and can be described by the equation
\[
\left( \frac{V_0}{V} \right)^2 - \frac{1}{\pi} \left( \frac{\alpha \lambda}{V} \right) = \left( \frac{V_0}{V} \right)^2 \omega^{-\infty} + \left[ \left( \frac{V_0}{V} \omega^{-\infty} \right) \right]^{-1} \left( \frac{V_0}{V} \right)^2 \omega^{-\infty} + \left[ \left( \frac{V_0}{V} \omega^{-\infty} \right) \right]^{-\beta}
\]
(5)

where indexes \( \omega^{-\infty} \) and \( \omega^{-\infty} \) refer to \( \omega \tau \ll 1 \) and \( \omega \tau \gg 1 \); \( \tau \) is limiting relaxation in equation (4) and effective one in equation (5); \( \beta = \frac{2\theta}{\pi} \) is empirical parameter, characterizing the distribution of relaxation times (\( 0 \leq \beta \leq 1 \)), \( \theta \) means the angle between the diagram abscissa and the straight line, connecting the centre of the curve with point \( \left( \frac{V_0}{V} \omega^{-\infty}, 0 \right) \).

Thus, the analysis of experimental results on the sound absorption and velocity shows that acoustic dispersion observed in \( CS_2 \) is characterized by one relaxation time, and the acoustic dispersion observed on \( C_6H_6, C_5H_5N, CH_2Cl_2, CH_2Br_2, C_4H_4S \) is characterized by several relaxation times.

It may be assumed, that the acoustic relaxation in \( C_6H_6, \) \( CS_2, \)
Acoustic Dispersion and its Mechanism in Benzene, Pyredine, 
Chlorifirm and some other Liquids in frequency range 10 - 5000 Mc/s

\[\text{C}_2\text{H}_5\text{N}, \text{CHCl}_3, \text{C}_4\text{H}_4\text{S}, \text{CH}_2\text{Cl}_2, \]
\[\text{CH}_2\text{Br}_2\] takes place due to excitation of all molecule normal vibrations. The process of excitation of inside molecule vibrations for all investigated liquids, probably, takes place successively through the lowest mode.

\[\text{Fig. 3. Dependence of } \frac{\alpha^2}{\frac{V_0}{V}} \text{ on } \left(\frac{V_0}{V}\right)^2 \text{ for liquids } \text{C}_6\text{H}_6, \text{C}_5\text{H}_5\text{N}, \]
\[\text{CHCl}_3, \text{C}_4\text{H}_4\text{S}, \text{CH}_2\text{Cl}_2 \text{ and } \text{CH}_2\text{Br}_2. \]
* - Author's results of hyperaoustic measurements.
□, ○, Δ, O, X - Author's results of ultrasonic measurements.
+ - I.L. Fabelinsky's data.

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<tr>
<th>Liquids</th>
<th>t°C</th>
<th>A × 10^-17</th>
<th>B × 10^-10</th>
<th>C/10</th>
<th>V_0</th>
<th>V_0d</th>
<th>V_G</th>
<th>f G</th>
<th>C_p</th>
<th>C_v</th>
<th>C'</th>
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<td>-</td>
<td>-</td>
<td>18.16</td>
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<td>17.03</td>
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— J-48 —
Acoustic Dispersion and its Mechanism in Solutions of Carbon Disulphide - Benzene and Pyridine - Benzene in the Frequency Range 10-1000 Mc/sec

Moscow State University

The aim of the present paper is to obtain experimental data about the acoustic properties of the system CS$_2$ - C$_6$H$_6$, C$_5$H$_5$N - C$_6$H$_6$, over a frequency range of 10 to 1000 Mc/sec, and to compare this data with predict of the vibration relaxation theory.

Sound absorption and velocity measurements were carried out by the pulse method of variable distance. With high frequencies non-resonance excitation of the monocystal surface, placed into the gap of resonance cavity was employed.

The results of our experiment can be described with the following formula:

$$\alpha = B + \frac{A}{1 + \omega^2 \tau^2}$$

(1)

The experimental values of $A$, $B$, $\tau$ and the value of $C_p$ which means specific heat at constant pressure and $C_v$ which means specific heat at constant volume, and $C'$ which means full vibrational specific heat calculated on the basis of the data on the vibrational spectrum CS$_2$, C$_5$H$_5$N, C$_6$H$_6$, are given in the Table. As the formula (1) does not give any definite answer to the question whether one or several relaxation times are present in the solutions CS$_2$ - C$_6$H$_6$.
Acoustic Dispersion and its Mechanism in Solutions of Carbon Disulphide - Benze and Pyridine - Benze in the Frequency Range 10 - 1000 Mc/sec

C₅H₅N - C₆H₆, it will be useful to apply some other methods in description of experimental results in the field of acoustic dispersion.

The method suggested by Kneser is one used for the purpose.

According to Kneser

\[
\left( \frac{\alpha' \lambda}{\pi} \cdot \frac{V_0^2}{V^2} \right)^2 + \left( \frac{V_0^2}{V^2} - \frac{V_0^2}{2V_0^2} \right)^2 = \left( \frac{V_0^2 - V_0^2}{2V_0^2} \right)^2
\]  

(2)

Where \( \alpha' \) means sound excessive absorption; \( \lambda \) is sound wavelength; \( V_0 \), \( V \) and \( V_\infty \) are sound velocity at frequencies \( \omega = (2\pi\nu) \rightarrow 0 \), \( \omega = (2\pi\nu) \rightarrow \infty \), respectively.

The values of \( V_0 \) and \( V_\infty \) are presented in the Table.

If the values \( \frac{\alpha' \lambda}{\pi} \cdot \left( \frac{V_0}{V} \right)^2 \) are plotted on the ordinate axis and the values \( \left( \frac{V_0}{V} \right)^2 \) are laid off on the abscissa, the experimental points on the diagram form a half circle with the centre on the abscissa in case of one relaxation time.

If the distribution of relaxation times takes place, the diagram differs widely from a half circle and is similar to Davidson and Cole or Cole and Cole diagrams (Fig. 1; 2).

In this case the acoustic relaxation may be written by the following formula:

\[
\frac{V_0}{V} = 1 \left( \frac{\alpha' \lambda}{\pi} \cdot \frac{V_0^2}{V^2} \right) + \left( \frac{V_0}{V} \right)^2 + \left[ \frac{V_0}{V} \right]_{\omega \rightarrow \infty} \left[ 1 + i\omega \tau_0 \right]^{-\beta}
\]  

(3)

and

\[
\left( \frac{V_0}{V} \right)^2 - i \left( \frac{\alpha' \lambda}{\pi} \cdot \frac{V_0^2}{V^2} \right) = \left( \frac{V_0}{V} \right)^2 + \left[ \frac{V_0}{V} \right]_{\omega \rightarrow \infty} \left( \frac{V_0}{V} \right)^2 \left[ 1 + i\omega \tau_0 \right]^{-\beta}
\]  

(4)

where \( \tau_0 \) means the limiting relaxation time in equation (3) and in equation (4) it means the effective relaxation time; \( \beta = \frac{2\psi}{\pi} \) is empirical parameter, characterizing the distribution of relaxation times \( 0 < \beta < 1 \); \( \psi \) means the angle between abscissa of the diagram and a straight line, connecting the centre of the curve with the point \( \left( \frac{V_0}{V} \right)_{\omega \rightarrow \infty}, 0 \).

Thus, the analysis of the experimental data shows that the acoustic relaxation observed in solutions CS₂ - C₆H₆; C₅H₅N - C₆H₆

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is characterized by several relaxation times.

It may be assumed, that the acoustic relaxation in solutions $\text{CS}_2 - \text{C}_6\text{H}_6$, $\text{C}_5\text{H}_5\text{N} - \text{C}_6\text{H}_6$ takes place due to excitation of all molecule normal vibrations. The process of excitation of vibrations inside molecule for all investigated solutions, probably, takes place successively through the lowest mode.

Table

Acoustical Properties of Solutions of the Pyridine - Benzene at 25°C

<table>
<thead>
<tr>
<th>Content of Pyridine in Benzene on Mole Fraction</th>
<th>$A \cdot 10^{17}$ sec$^{-2}$ cm</th>
<th>$B \cdot 10^{17}$ sec$^{-2}$ cm</th>
<th>$\tau \cdot 10^{-10}$ sec</th>
<th>$C_p$, cal mol$^{-1}$ deg</th>
<th>$C_v$, cal mol$^{-1}$ deg</th>
<th>$C'$, cal mol$^{-1}$ deg</th>
<th>$V_o'$, cm sec</th>
<th>$V_{\infty}'$, cm sec</th>
</tr>
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<tbody>
<tr>
<td>0.0</td>
<td>900</td>
<td>9</td>
<td>2.61</td>
<td>33.9</td>
<td>23.3</td>
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<td>1576</td>
</tr>
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</table>

Acoustical Properties of Solutions of the Carbon Disulphide - Benzene at 25°C

<table>
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<tr>
<th>Content of Carbon Disulphide in Benzene on Mole Fraction</th>
<th>$A \cdot 10^{17}$ sec$^{-2}$ cm</th>
<th>$B \cdot 10^{17}$ sec$^{-2}$ cm</th>
<th>$\tau \cdot 10^{-10}$ sec</th>
<th>$C_p$, cal mol$^{-1}$ deg</th>
<th>$C_v$, cal mol$^{-1}$ deg</th>
<th>$C'$, cal mol$^{-1}$ deg</th>
<th>$V_o'$, cm sec</th>
<th>$V_{\infty}'$, cm sec</th>
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<td>0.0</td>
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<td>8</td>
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<td>11.71</td>
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Acoustic Dispersion and its Mechanism in Solution of Carbon Disulphide - Benzene and Pyridine - Benzene in the Frequency Range 10 - 1000 Mc/sec

Fig.1. Dependence of \( \frac{\alpha' \lambda}{\pi} \left( \frac{V_0}{V} \right)^2 \) on \( \left( \frac{V_0}{V} \right)^2 \) in Solutions of Pyridine - Benzene

Curve 1 - Benzene; 2, 3, 4 - 0.3; 0.5; 0.7 of Pyridine in Benzene, respectively; 5 - Pyridine.

- Author's results at hyperacoustical measurements
- I.L. Fabelinsky's data

Fig.2. Dependence of \( \frac{\alpha' \lambda}{\pi} \left( \frac{V_0}{V} \right)^2 \) on \( \left( \frac{V_0}{V} \right)^2 \) in Solutions of Carbon Disulphide - Benzene

Curve 1 - Carbon Disulphide; 2, 3, 4, 5, 6 - 0.1; 0.3; 0.5; 0.7; 0.9 - of Benzene in Carbon Disulphide, respectively; 7 - Benzene.

- I.L. Fabelinsky's data
Viscoelastic Relaxation of some Supercooled Liquids

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Department of Chemistry, University of Essex, Colchester, England.

At high frequencies of alternating shear stress, liquids show viscoelastic behaviour: with increasing frequency the dynamic viscosity decreases while the rigidity modulus increases and attains a limiting value \( G_\infty \) at frequencies above the viscoelastic relaxation region. In a liquid such as water where the viscosity is about 1 centipoise, the relaxation time \( \tau \) for flow of molecules in the liquid is about \( 10^{-12} \) second. In order to observe the relaxation region with the available frequencies of 5, 10 and 30 MHz, it is necessary to supercool the liquid to a viscosity greater than 10 poise. We have studied the viscoelastic behaviour of a number of supercooled hydrocarbon liquids and their derivatives in order to investigate the effect of molecular structure on viscoelastic relaxation.

The experimental work has been carried out using a normal incidence technique in which a pulse of shear waves is propagated along a fused quartz delay line, and the reflection coefficient at the quartz-liquid interface determined.\(^1\) From this the real part of the shear mechanical impedance of the liquid \( R_L \) is obtained. Since the range of frequencies available is small, it has been effectively extended by altering the temperature of the liquid.

Fig. 1 shows the variation with temperature of \( \frac{R_L^2}{\rho} \) for sec-butyl cyclohexane, where \( \rho \) is the liquid density. At low temperatures the results for the three frequencies coalesce, and this region corresponds to the non-relaxing \( G_\infty \). At higher
temperatures, the results at the three measuring frequencies diverge in the relaxation region. In order to remove the non-relaxing contribution from the relaxation region, it is necessary to extrapolate \( G_\infty \) using the plot of \( \rho/R_L^2 \) against temperature in Fig. 2. As has previously been observed for other substances, the non-relaxing part of this graph varies linearly with temperature. For this linear portion to represent \( G_\infty \) unambiguously an accurate determination of the glass transition temperature \( T_g \) must be available and the onset of the relaxation region should be defined by at least two frequencies. \( T_g \) has been determined by differential thermal analysis.

Fig. 1 Variation with temperature of \( R_L^2/\rho \) for sec-butyl cyclohexane; \( T_g \) = glass transition temperature.

Fig. 2 Linear variation of \( 1/G_\infty \) with temperature for sec-butyl cyclohexane; \( T_g \) = glass transition temperature.
Viscoelastic Relaxation of some Supercooled Liquids

The extrapolated $G_\infty$ values from Fig. 2 may be used to obtain the viscoelastic relaxation region of sec-butyl cyclohexane shown in Fig. 3. The curve is significantly broader than that of a single Maxwell relaxation time. It cannot be described by the empirical Cole-Cole or Cole-Davidson expressions, although it is moderately well described by a Gaussian distribution of relaxation times. The theory of Barlow, Erginsav and Lamb, in which the shear mechanical impedance of a viscoelastic liquid is represented by a parallel combination of the impedances of a Newtonian liquid and a Hookean solid, is also not in agreement with the results for sec-butyl cyclohexane. The latter theory does provide a good description of the relaxation region of $n$- and iso-propyl benzene, but not of sec-butyl benzene, 2-phenyl ethyl chloride, 3-phenyl propyl chloride or 3-phenyl propanol.

As temperature increases and more free-volume becomes available for molecular motion, the width of the viscoelastic and dielectric relaxation regions of liquids decreases. The results for the liquids studied here show that the width of the viscoelastic relaxation region of supercooled liquids is also dependent upon

![Fig. 3 Viscoelastic relaxation region of sec-butyl cyclohexane; line drawn through points is sum of three Maxwell curves, $\tau_1$, $\tau_2$ and $\tau_3$.](image)

molecular structure. The relaxation regions of the liquids investigated can be adequately represented by summing three Maxwell single relaxation times corresponding to three mutually perpendicular translational motions (Fig. 3). There is, however, no obvious correlation between the ratio of the relaxation times for a particular substance and its molecular structure if only translational motion is
Viscoelastic Relaxation of some Supercooled Liquids

considered.

It is likely that overall molecular rotation and internal molecular rotation play a significant part in determining the case of translational motion of a molecule and hence the width of the relaxation region. At high temperatures molecular rotation in a liquid occurs more often than molecular translation so that an asymmetric molecule can translate equally readily in any direction.\(^5\) this leads to the narrow distribution of relaxation times. In the supercooled region, however, overall molecular rotation occurs less readily than molecular translation\(^5\), and a broad distribution of relaxation times is observed.

The activation energy for viscous flow in the relaxation region of the liquids under investigation is typically 15 kcal/mole. This is significantly larger than the energy required to convert one molecular conformation into another (typically 5 kcal/mole). If a number of conformations are accessible to a translating molecule, then it might be expected that such a flexible molecule would have a narrower distribution of shear relaxation times than a similar rigid molecule. This is in reasonable agreement with the observed width of the distribution of relaxation times: sec-butyl cyclohexane < 3-phenyl propyl chloride < 2-phenyl ethyl chloride = sec-butyl benzene < n-propyl benzene = iso-propyl benzene < 3-phenyl propanol. The major exception is 3-phenyl propanol, where molecular association as a result of hydrogen-bonding is likely to broaden the relaxation region.

Phase transition to a liquid crystalline phase, studied by ultrasound.

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Department of Biomedical Engineering
Moore School of Electrical Engineering
University of Pennsylvania
Philadelphia, Pa., 19104

Fig 1 shows the phase diagram for the system octylamine - water. The critical conditions for transition from an isotropic liquid (1) to a nematic liquid crystal (5) are $T_c = 35.6 \pm 0.2^\circ C$ and $C_c = 0.856$ mole fraction water ($0.144$ mole fraction octylamine). Ultrasonic absorption coefficients, $\alpha$, and velocities of propagation, $v$, have been measured with pulse apparatus over the full range of concentration, frequency range $f = 10 - 130$ MHz and temperature range $T = 31 - 42^\circ C$. The results shows a cusp in absorption coefficient and a discontinuity in velocity of propagation in the region of phase transition. This behavior is similar to that of other systems in the vicinity of a critical point, i.e. gas-liquid or binary liquid systems.

The results now reported constitute the first ultrasonic measurements obtained for a two-component system undergoing phase transition to a liquid crystalline state.

Aldrich #0-580-2 or Eastman Kodak #P7588, practical grade octylamine was distilled twice in a 47 cm. packed column. Glass-distilled water, pH = 7, was used. Samples were prepared immediately before measurement and were maintained in an atmosphere of nitrogen. Thermal stability was $\pm 0.1^\circ C$.  

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Phase transition to a liquid crystalline phase, studied by ultrasound.

Fig 2 shows velocity and absorption parameter, $\alpha/t^2$, as a function of temperature at the critical concentration.

Fig 3 shows the frequency dependence of $\alpha/t^2$ at the critical concentration. $T_c = 31.8^\circ C$ indicated an undistilled impure sample. However, relaxational behavior is indicated; it is described by more than one time constant, including probable magnitudes greater than 0.02 $\mu$sec (relaxation frequencies $<10$ MHz). Diffusion controlled processes may be inferred. Fig 4 shows the dependence of velocity on concentration and temperature at 10 MHz. The curves must cross one another to terminate at McSkimin's\(^2\) data for pure water. Such crossing (and maxima in velocity at high concentrations of water) have already been observed in the case of methyl diethylamine-water in the temperature range 0-39$^\circ C$ and explained in terms of breakdown of water structure.

Fig 5 shows the dependence of $\alpha/t^2$ on concentration and temperature at 10 MHz. $T = 36.85^\circ C$ is closest to critical conditions. Data referring to lower temperatures and concentrations in the vicinity of $C_c$ are for the nematic liquid crystalline phase; these particular data are preliminary. The subsidiary peak at high concentrations of water and 31.1$^\circ C$ may indicate the formation of micellar structures on approach to the phase boundary between phase (1) and the two-phase region (9)\(^3\). Data obtained in previous investigations have been used to construct the curve for 31.1$^\circ C$\(^4\). At higher frequencies changes are less pronounced and the peaks in $\alpha/t^2$ appear to shift to lower concentration of water.

\(^{(*)}\) J.F. McKellar and J.H. Andreae, Nature 195, 865-7 (1962)

This work was supported by NSF Grants GK-440 and GK-1964.
Phase transition to a liquid crystalline phase, studied by ultrasound.

Fig. 1. Phase diagram for octylamine-water (after Ralston et al., JACS, 64 (1942) 1516).

Fig. 2. Velocity ($v$) and absorption parameter ($\alpha$) at 10 MHz in the critical region for octylamine-water.

Fig. 3. Frequency dependence of $\alpha/f^2$ for an impure sample of octylamine-water in the nematic region ($T - T_c < 0$) and in the critical region ($T - T_c > 0$).
Phase transition to a liquid crystalline phase, studied by ultrasound.

![Graph 1: Dependence of velocity of sound upon concentration and temperature for octylamine-water](image)

**Fig. 4.** Dependence of velocity of sound upon concentration and temperature for octylamine-water

![Graph 2: Dependence of $\alpha/r^2$ upon concentration and temperature for octylamine-water](image)

**Fig. 5.** Dependence of $\alpha/r^2$ upon concentration and temperature for octylamine-water
Ultrasonic Absorption in Detergent Solutions
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Professor, Graduate Student and Professor of
Department of Chemistry, Faculty of Science,
Hiroshima University

Introduction

Less attention\textsuperscript{1,2,3,4} has been paid to the kinetics of micelle formation nevertheless the extensive studies on the detergents have been done on their physical and chemical properties.

Recently the present authors\textsuperscript{5} have found the absorption near 100 Kc at the concentration higher than critical micelle concentration (CMC) for sodium dodecyl sulphate (SDS) solution, have assigned the absorption mechanism to the volume relaxation related to the dissociation–recombination reaction between micelle and counterion from quantitative agreement between theory and experiments and further have calculated the characteristics on its kinetics.

The purpose of the present investigation is to determine the mechanism of absorption in fatty acid soap solutions and to discuss the kinetic parameters on the basis of length of hydrocarbon chain.

Experiment and Results

The measurement of ultrasonic absorption were made at the various concentrations of sodium caproate, caplyrate and caprate by the pulse method over the frequency range from 5 to 95 Mc as described in detail elsewhere.\textsuperscript{6}
Ultrasonic Absorption in Detergent Solutions

Figure 1 shows the typical absorption spectra where the observed values are plotted on the curve expressed by the equation applicable to single relaxation. For these solutions the absorption was observed only at the concentration higher than their CMC. Even at the concentration lower than CMC the solution showed absorption by an addition of salt.

Let us assume the following dissociation-recombination equilibrium between micelle and counterion in solution as an absorption mechanism:

\[ M' \rightleftharpoons M' + nNa^+ \]  \hspace{1cm} (I)

where \( M' \) and \( M'' \) are two types of micelles. If it is assumed that the counterion reaches the buffer equilibrium rapidly enough with its concentration constant during the perturbation by the sound pressure, one obtains the next equation:

\[
\beta' = \frac{\beta_r}{1 + i\omega} = \frac{(\Delta V^0)^2}{\gamma RT} \cdot \frac{C_{\text{M}} + C_{\text{M}''}}{C_{\text{Na}^+} K + C_{\text{Na}^+}^n + 2} \cdot \frac{1}{1 + i\omega} \]  \hspace{1cm} (1)

where \( \beta' \) is the complex compressibility, \( \beta_r \) the relaxational compressibility, \( \Delta V^0 \) the partial molal volume change for the reaction, \( K \) the equilibrium constant, and \( \tau \) the relaxation time. The relaxational compressibility can be calculated by

\[
\beta_r = \frac{2(\alpha\lambda)_{\text{max}}'}{\pi\rho v^2} \]  \hspace{1cm} (2)

where \( (\alpha\lambda)'_{\text{max}} \) is the absorption coefficient per wave length at the relaxation frequency, \( \rho \) the density of solution, and \( v \) the velocity of sound.

Eq. (1) means that the plot of \( (C_{\text{M}} + C_{\text{M}''})/\beta_r \) vs \( C_{\text{Na}^+} \) has a minimum at \( C_{\text{Na}^+} = K \).
With assumption
\[ C_M' + C_M'' = C_E/m = (C - C_s)/m \]  \[ C_{Na^+} = \delta C \]  
\[ C_E/\beta_r \] values obtained by experiment are plotted against C in Fig. 2, where C is the concentration of surfactant, C_s the CMC, m the aggregation number of surfactant molecule in a micelle, and \( \delta \) the constant. In the curve the minimum yields \( 4(\Delta V^o)^2/\gamma RT \) and its concentration is equal to \( K/\delta^N \). The solid lines are the theoretical curves calculated under the parameter of n using the values for \( 4(\Delta V^o)^2/\gamma RT \) and \( K/\delta^N \) obtained from the experimental data.

The experimental data fall well on the theoretical curves at n = 3 for sodium caprylate. This verifies that the mechanism of absorption in detergents can be attributed to the reaction (I). According to this reaction the relaxation frequency is related to the rate constants as follows:

\[ 2\pi f_r = k_f + k_b C_{Na^+}^n = kk_b + k_b C_{Na^+}^n \]  
The extrapolation of the curve to concentration zero gives the value for \( k_f \). Using the values for \( K/\delta^n \), \( n \) and \( k_f \) obtained by the above consideration and 0.5 for \( \delta \) of sodium caprylate obtained by McBain, the value for \( k_b \) was calculated from \( K = k_f/k_b \). This is shown in Table I together with the other kinetic values including those for SDS. With assumption \( K \ll C_{Na^+}^n \) Eq.(1) can be approximately rewritten as follows:

\[ \gamma n \frac{\delta_r T}{C_E} = \ln \frac{(\Delta V^o)^2}{\gamma m R} \cdot \frac{1}{C_{Na^+}^n} + \frac{\Delta S}{R} - \frac{AH}{RT} \]  

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Ultrasonic Absorption in Detergent Solutions

The values for $\Delta H$ and $\Delta S$ are tabulated in Table I along with the value for $\Delta F$ calculated through $\Delta F = \Delta H - T\Delta S$ with the assumption that $\Delta V^0$, $\gamma$ and $\Gamma$ are constant independent of temperature.

**Table I** Characteristics on the Kinetics for the Dissociation-Recombination Reaction between Micelle and Counterion at 30°C

<table>
<thead>
<tr>
<th></th>
<th>Sodium caprate</th>
<th>Sodium caprylate</th>
<th>Sodium caprate</th>
<th>SDS$^5$</th>
<th>Octylamine hydrochloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>2.0 $\times$ 10$^{-1}$</td>
<td>1.1 $\times$ 10$^{-2}$</td>
<td>4.1 $\times$ 10$^{-3}$</td>
<td>1.8 $\times$ 10$^{-5}$</td>
<td>8.6 $\times$ 10$^{-3}$</td>
</tr>
<tr>
<td>$\Delta F$, kcal/mole</td>
<td>1.0</td>
<td>2.7</td>
<td>3.3</td>
<td>6.6</td>
<td>2.9</td>
</tr>
<tr>
<td>$\Delta H$, kcal/mole</td>
<td>-3.0</td>
<td>-1.5</td>
<td>-3.0</td>
<td>-2.7</td>
<td></td>
</tr>
<tr>
<td>$\Delta S$, c.u.</td>
<td>-19.3</td>
<td>-15.9</td>
<td>-18.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_r$, sec$^{-1}$</td>
<td>1.2 $\times$ 10$^8$</td>
<td>3.8 $\times$ 10$^7$</td>
<td>1.1 $\times$ 10$^7$</td>
<td>1.5 $\times$ 10$^5$</td>
<td>1.8 $\times$ 10$^7$</td>
</tr>
<tr>
<td>$k_b$, kcal/mole sec$^{-1}$</td>
<td>0.6 $\times$ 10$^9$</td>
<td>3.3 $\times$ 10$^9$</td>
<td>2.8 $\times$ 10$^9$</td>
<td>8.4 $\times$ 10$^9$</td>
<td>2.1 $\times$ 10$^9$</td>
</tr>
</tbody>
</table>

References
Ultrasonic Absorption in Polymer Solutions

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Faculty of Engineering,
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The absorptions of ultrasonic waves in polymer solutions were studied. The measurements of ultrasonic absorption were made by the pulse-echo method. The apparatus used were similar to those reported previously(1,2). The block diagram and the measuring cell used were shown in Fig. 1 and 2, respectively. The measuring frequencies were from 3 to 60 mega cycles/sec. The polymer solutions studied were: poly-(methylmethacrylate) in toluene, polystyrene in toluene, and methylcellulose in water. The results obtained were summarized as follows.

1. Concentration dependence of absorption coefficient

The absorption coefficient of ultrasonics in the solution of poly-(methylmethacrylate) (molecular weight 10^6) in toluene increased almost linearly with the increase of concentration of the polymer, and the slope of the increase became small when the frequency increased.

In the plots of absorption coefficients against the concentrations for the solutions of methylcellulose in water and polystyrene in toluene, break points were observed. The concentrations of the polymers at which the breaks occurred shifted to the lower concentration side when
Ultrasonic Absorption in Polymer Solutions

the molecular weight of the polymer was increased.

The relation between the concentration of break point and the frequency was examined for the solutions of polystyrene (molecular weight $2 \times 10^5$) in toluene at the frequencies from 5 to 44 mega cycles/sec. The concentration of break point was inversely proportional to the frequency. These break points were ascribed to the onset of the entanglement of the polymer molecules. Above the concentration of break point, the absorption of ultrasonics became independent of the molecular weight of the polymer.

2. The temperature change of the ultrasonic absorption

The temperature change of ultrasonic absorption was examined for the solutions of polystyrene (molecular weight $2 \times 10^5$) in toluene. The concentrations of polymer were 4, 6, and 8 weight per cent, and the measuring temperatures ranged from -10 to 30°C. The results are shown in Figs. 3 and 4. The complicated behaviors of the temperature change are due to the entanglement of the polymer molecules.

The absorption coefficient of solution of poly-(methylmethacrylate) in toluene relative to the pure solvent was represented by a relaxation equation of single relaxation time over wide ranges of temperatures and concentrations.
Ultrasonic Absorption in Polymer Solutions

Fig 3

Fig 4

References
2) H. Nomura, S. Kato, and Y. Miyahara, Ibid., 89, 149 (1968)
Determination of the Rotational Potential of Polystyrene by Sound Absorption Measurements in Solutions

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Germany

Introduction:
In the years 1960-1962 Cerf, Zana, and Candau \(^1\) published measurements of ultrasonic absorption in solutions of polystyrene in benzene with a sudden decrease of \(\alpha\) by 8 to 12 percent within a small frequency region at 3 Mcps. This change is not explainable by any relaxation process \(^2\). Since that steep decrease was not found in other solvents, we repeated the measurements. Our apparatus had some advantages for measurements in the low megacycle range compared to the one used by Cerf et al.: It was pulsed instead of CW, thus we had not to use the Musa method. The transducers were of the Sell type, which means broad band action and a better sound field. The latter fact is of especial importance since in that low frequency range the small absorptions are superimposed by diffraction effects. Those could be corrected for in a reliable way by the method of Bass \(^3\), as test measurements in the pure solvents did show. In addition the circuitry was stable enough within the time necessary for one run (approximately 1 min because of an automatic recording) to measure absorptions of 0.05 dB/cm with 5 percent accuracy.

Experimental Results:

Fig. 1 shows the results obtained in a 4 percent solution at 20°C (more exactly 4 g PST in 100 cm\(^3\) of the solvent).

Apparently the sudden step was not found, rather we were inclined to explain the small deviation of \(\mu\) from the 45° line (---, caused by viscosity of the solvent and vibrational relaxation of the solution) by a single relaxation process. Plotting, as usual, this excess absorption \(\Delta\alpha\) alone (Δ), it could be fitted by a Debye absorption curve (-----) within the accuracy of the measurement. This fitting could be done very well by a numerical method developed by one of us (H.-J. B.). Although our interpreta-
tion is totally different, the measurements of Cerf et al. \(^4\) do not deviate very much from the ours except the sudden step. The single relaxation shows up much more clearly in measurements in the solvent CCl\(_4\) (fig. 2), since the 45° part of \(\mu\) is smaller than in benzene. Again a single Debye curve could be fitted to the excess absorption for two sets of measurements, namely in a technical PST with a broad distribution of molecular weight (o), \(M \approx 200\,000\), and a narrow dispersed PST (●), \(M = 430\,000\). Apparently there is only a negligible influence of the chain length on the process.

---

**Fig. 2**: Dependence on Molecular Weight

To associate the relaxation with an internal process, first the concentration dependence has been studied. Fig. 3 shows the Debye excess absorption in three mixtures (5, 10, and 20 percent) at the same temperature (20°C). One easily sees the excess absorption to be proportional to the concentration, as expected. Much more interesting is the temperature dependence, shown in the same figure for the 10 percent solutions: An increase of \(T\) causes a shift to higher frequencies (Arrhenius behaviour) and a decrease of \(\mu_{\text{max}}\).

**Discussion:**

Considering the relaxation process to be a thermal one — i.e. rejecting viscous or mere compressional relaxation —, the relaxing part of the heat capacity \(\delta C\) can be calculated from the \(\mu_{\text{max}}\) as usual \(^5\):

\[
\delta C \approx (2k\mu_{\text{max}}/\tau) \frac{C_p^0 C_p}{(C_p - C_v)}.
\]

The results, related to one mole of monomer unit, are given in table 3, 3rd column. Now a process has to be looked for, of which the heat capacity contribution decreases with increasing temperature. It is easily found in a rotational isomerism within the polymer chain. The formalism of rotamer relaxation in low molecular weight substances \(^6\) must be modified only slightly: A single rotation from a trans into a gauche position would force the chain molecule either to move by a large angle through the solvent or to bend strongly, whilst an
additional opposite rotation of the next but one C–C bond -- a so-called "kink" conformation -- causes only a slight shift of the left to the right part of the polymer chain (fig. 4). Therefore the rotational potential in fig. 5 must be understood to be for the sum of these two rotations. If the process happens at the most once in every monomeric unit, the equilibrium between 1 and 2 contributes to the molar heat capacity a Schottky part

$$\delta C/R = (\Delta H/RT)^2 \alpha e^{-\Delta H/RT} / (1 + \alpha e^{-\Delta H/RT})^2$$

which shows a maximum at about $\Delta H/RT \approx 2.5$ and a decrease with $T$ at the high temperature side. Assuming $\alpha = 2$ (two-fold degeneracy of the gauche position and neglect of the change in vibrational entropy), from the experimental $\delta C$ the energy difference $\Delta H$ could be calculated (4th column of table 1). The good agreement between the various systems confirms the interpretation given. Thus the mean energy difference between the regular and "kinked" conformation is $\Delta H = (0.88 \pm 0.12)$ kcal/mole.

Not only the energy difference of the two states but also the potential barrier $\Delta H_{21}$ between can be derived from the measurements. The transition rate $\Gamma_{21}$ was calculated from the positions of the maxima $I_{\text{max}}$ by

$$\Gamma_{21} = 2\pi I_{\text{max}}/(1 + \alpha e^{-\Delta H/RT})$$

Fig. 6 shows an Arrhenius plot of $\Gamma_{21}$ for two mixtures. One obtains the activation energies $\Delta H_{21} = 6.6$ kcal/mole, $\Delta H_{12} = 7.5$ kcal/mole, and a frequency factor of $1.4 \times 10^{12}$ s$^{-1}$.

Conclusion: It has been shown that the transition between a "kink" and a regular conformation of a polymer chain contributes to the sound absorption of a polymer solution, and that the investigation of the temperature dependence of $I_{\text{max}}$ and $\Gamma_{21}$ allows the
Rotational Potential of Polystyrene from Sound Absorption in Solution

determination of the rotational potential.

Acknowledgements:
The authors are indebted to Dr. W. Pechhold for discussions on kink isomers.

<table>
<thead>
<tr>
<th></th>
<th>T [°C]</th>
<th>( \omega_{\text{max}} \times 10^3 )</th>
<th>( \Delta C/R )</th>
<th>( \Delta H ) [kcal/mol]</th>
<th>c [m/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄ + 5 percent PST 430 000</td>
<td>10°</td>
<td>1.08</td>
<td>0.56</td>
<td>0.96</td>
<td>985</td>
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<tr>
<td>&quot;</td>
<td>20°</td>
<td>0.83</td>
<td>0.43</td>
<td>0.82</td>
<td>951</td>
</tr>
<tr>
<td>&quot;</td>
<td>35°</td>
<td>0.61</td>
<td>0.32</td>
<td>0.71</td>
<td>906</td>
</tr>
<tr>
<td>CCl₄ + 10 percent PST IIIC (BASF)</td>
<td>35°</td>
<td>1.97</td>
<td>0.56</td>
<td>0.92</td>
<td>1027</td>
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<td>20°</td>
<td>1.77</td>
<td>0.50</td>
<td>0.90</td>
<td>969</td>
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<td>1.57</td>
<td>0.44</td>
<td>0.89</td>
<td>909</td>
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<td>&quot;</td>
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<td>0.41</td>
<td>0.90</td>
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<td>0.44</td>
<td>0.83</td>
<td>954</td>
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<tr>
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<td>20°</td>
<td>3.70</td>
<td>0.64</td>
<td>1.11</td>
<td>1002</td>
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<tr>
<td>C₆H₆ + 4 percent PST 152 000</td>
<td>9°</td>
<td>0.80</td>
<td>0.60</td>
<td>1.00</td>
<td>1362</td>
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<tr>
<td>&quot;</td>
<td>20°</td>
<td>0.75</td>
<td>0.56</td>
<td>0.98</td>
<td>1325</td>
</tr>
<tr>
<td>C₆H₆ + 10 percent PST IIIC</td>
<td>20°</td>
<td>1.54</td>
<td>0.51</td>
<td>0.92</td>
<td>1335</td>
</tr>
</tbody>
</table>

Table 1: Compilation of Experimental Results.
The sound velocity c did not show up dispersion.

Literature:
4) H. Häuser, H.-J. Bauer, Kolloid-Z., in press.
7) W. Pechhold, S. Blasenbrey, S. Woermer, Kolloid-Z. 189, 14 (1963), and W. Pechhold, Kolloid-Z., in press.
Propagation d'une onde ultrasonore dans des bitumes.

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Introduction.

On a étudié en fonction de la température entre -30 et +150°C et de la fréquence entre 300 et 2000 kHz les constantes de propagation d'une onde ultrasonore longitudinale se propageant dans des bitumes. Pour cela on a utilisé une méthode par impulsion (1) pour les mesures de l'amortissement et une méthode de coïncidence pour les mesures de vitesse de propagation. Les caractéristiques des bitumes utilisés sont rassemblées dans le tableau suivant :

<table>
<thead>
<tr>
<th>Bitumes</th>
<th>T B et A</th>
<th>Pénét. à 25°C</th>
<th>Indice de pénétra.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>100</td>
<td>13,8</td>
<td>+ 4</td>
</tr>
<tr>
<td>II</td>
<td>Distillation 40/50</td>
<td>51,5</td>
<td>45</td>
</tr>
<tr>
<td>III</td>
<td>Distillation 180/220</td>
<td>38,5</td>
<td>191</td>
</tr>
<tr>
<td>IV</td>
<td>Soufflé 90/40</td>
<td>87</td>
<td>35</td>
</tr>
<tr>
<td>V</td>
<td>Craqué 95/1</td>
<td>98</td>
<td>2</td>
</tr>
</tbody>
</table>

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Propagation d'une onde ultrasonore dans des bitumes.

Résultats Expérimentaux.

On a tracé les variations de l'amortissement et des vitesses en fonction de la température. La figure 1 montre que $\alpha$ passe par un maximum prononcé. La valeur de ce maximum décroît avec la fréquence en même temps qu'il se déplace vers les basses températures. La figure 2 indique que les vitesses de propagation décroissent lorsque la température augmente. Dans la zone correspondant au maximum de l'amortissement, on note une dispersion sensible des vitesses ; cette dispersion disparaît aux hautes et basses températures. La zone de dispersion coïncide avec la zone de transition caoutchoutique des bitumes. Sur les courbes isothermes on constate que la vitesse augmente légèrement avec la fréquence. Ces résultats sont en accord avec ceux obtenus pour d'autres polymères (2).

Sur les figures (3) et (4) on a tracé l'amortissement $\alpha$ et la vitesse $v$ pour les bitumes étudiés et pour une fréquence de 1400 kHz. La température correspondant au maximum de $\alpha$ dépend du type de bitume. Pour les bitumes de distillation directe elle coïncide avec la température bille-anneau, pour ces derniers qui ont une susceptibilité thermique élevée la valeur du maximum de $\alpha$ est plus importante. Pour les vitesses les bitumes les plus durs possèdent une vitesse plus élevée.

On a calculé à partir des valeurs expérimentales de $\alpha$ et de $c$ les parties réelles et imaginaires du module complexe $E^* = E_1 + jE_2$, dans l'hypothèse où l'onde ultrasonore qui se propage est plane et si $c/\rho = 1$ on peut appliquer les formules réduites

$$E_1 = \rho c^2 \quad E_2 = \frac{2 \rho c^3 \alpha}{\omega}$$

On a tracé sur la figure 5 les courbes $E_2 = f(E_1)$ dans le plan complexe. Tous les points expérimentaux se placent sur une courbe unique indépendante de la fréquence et de la température (3).
Propagation d'une onde ultrasonore dans des bitumes.

En conclusion ces mesures confirment les résultats antérieurs (4). Elles mettent en évidence une dispersion de vitesse et un maximum d'absorption dans la zone de transition des bitumes. En étendant les mesures du côté des basses fréquences jusqu'à 50 kHz par exemple, on doit pouvoir déterminer le facteur de translation $a_T$ de la relation (WLF) et les énergies apparentes d'activation.

Bibliographie.
(1) J.L.GARNIER - Note C.R.P. n° 742 - Marseille.
Propagation d'une onde ultrasonore dans des bitumes.

**Fig. 2** \( V = f(T)_N \)
- \( N = 1.4 \text{ MHz} \)
- \( \Delta = TB \text{ et } A \)

**Fig. 3** \( \alpha = f(T)_N \)
- Bitume 90/40
  1. 1819 KHz
  2. 1429
  3. 934
  4. 473
  5. 309

**Fig. 4** \( V = f(T)_N \)
- Bitume 90/40
  a. 1819 KHz
  b. 1429
  c. 934
  d. 473
  e. 309

**Fig. 5** \( E_2 = f(E_1) \)
- Bitume 90/40

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Hypersonic Velocities in Ethanol-Water Mixtures

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Masayuki Yamazaki and Masaru Itō
Institute of Industrial Science,
University of Tokyo

Introduction

It is known that the ultrasonic velocity and attenuation in alcohol-water mixtures show characteristic maxima at particular concentrations, indicating a relaxational interaction between the components. In ethanol-water mixtures, Storey\(^1\) has found a relaxation frequency of about 100 MHz from the ultrasonic attenuation measurements. Recently, hypersonic dispersion in this system has been observed by the authors\(^2\) with the aid of stimulated Brillouin scattering technique. We report here the detailed temperature dependence of the hypersonic velocities in ethanol-water mixtures determined by the method of spontaneous Brillouin scattering.

Experimental Procedure

The experiment was performed with the backward scattering configuration. He-Ne laser light was passed through a small hole bored at the center of a mirror and was introduced into a temperature-controlled cylindrical glass cell of 50 cm long. The mirror was set obliquely against the laser beam. The backscattered light was reflected by the mirror and was passed through a Fabry-Perot etalon and the resulting spectrum was photographed. Since the central line of the spectrum was too strong to measure, only the separation of Brillouin doublets was measured to determine the Brillouin shift frequencies.
Hypersonic Velocities in Ethanol-Water Mixtures

Measurements of the index of refraction for Na-D line and the mean dispersion of the sample were made with an Abbe type refractometer. Then the index for laser light was calculated using Cauchy's dispersion formula.

The ethanol used was reagent quality (above 99.5 vol%). The water sample was de-ionized and then distilled.

In order to compare hypersonic velocities with ultrasonic values, ultrasonic velocities of the mixtures were measured by the pulse method at 2 MHz. Measurements were made at temperatures from 10°C to 40°C.

Results and Discussion

Fig.1 shows curves of sound velocity versus ethanol concentration observed at 10°C. Remarkable velocity dispersion appears at intermediate ethanol concentrations.

Velocity dispersions at various temperatures are shown in Fig.2. It is noticeable that the maximum dispersion occurs at an ethanol concentration of 40 wt% (or 20 mol%) and the dispersion curves are remarkably asymmetrical against the ethanol concentrations. The amount of dispersion decreases with increasing temperatures.

Measurements of hypersonic attenuation have not been made. However, it is interesting to note that, in our previous experiments, no stimulated Brillouin scattering occurred at the composition of 40 wt%, implying strong hypersonic absorptions.

The results of hypersonic measurements are tabulated in Table I and the ultrasonic data in Table II.

Relaxation theories for alcohol-water mixtures have been developed by Nomoto and Schneider in order to interpret their pronounced excess ultrasonic absorptions. Nomoto's model for ethanol-water system implies a relaxation frequency of about 100 MHz which has been found by Storey. An evaluation based on the two-state theory of Schneider was made by Kor and Verma predicting a relaxation frequency of 2 GHz at 0°C for this system. Recently, Stone and Pontinen has also shown a relaxation time of about 10^{-10} sec at 25°C. These theories, however, only predict rather symmetrical
Hypersonic Velocities in Ethanol-Water Mixtures

Fig. 1 Ultrasonic and hypersonic velocities in ethanol-water mixtures at 10°C. Numbers in the figure show observed Brillouin shifts in GHz.

Fig. 2 Velocity dispersions in ethanol-water mixtures at various temperatures. A typical experimental error is shown with a vertical bar.
Table I Observed hypersonic velocities and frequencies in ethanol-water mixtures.

<table>
<thead>
<tr>
<th>Ethanol wt%</th>
<th>10°C m/s</th>
<th>10°C GHz</th>
<th>20°C m/s</th>
<th>20°C GHz</th>
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<td>6.4</td>
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<td>6.5</td>
<td>1559 ± 6</td>
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<td>6.6</td>
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<td>1613 ± 6</td>
<td>6.9</td>
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<td>1637 ± 8</td>
<td>7.0</td>
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<td>1129 ± 5</td>
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Table II Ultrasonic velocities in ethanal-water mixtures observed at 2 MHz.

<table>
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<tr>
<th>Ethanol wt%</th>
<th>10°C m/s</th>
<th>20°C m/s</th>
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<td>1095</td>
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</tbody>
</table>

References
Dispersion and Attenuation of Sound in a Highly Concentrated Suspension (1968)
Joseph C. F. Chow
Assistant Professor of Fluid Mechanics,
University of Illinois at Chicago Circle
Chicago, Illinois, U.S.A.

Introduction

The dispersion and attenuation of acoustic waves in a two-phase medium has attracted much attention in the past. The first serious analytical attempt was made in 1910 by Sewell(1) who computed the energy dissipation due to the viscous interaction between rigid particles and an oscillating incompressible fluid for a low volume particle concentration. This work was extended by Epstein(2) and Ratinskaga(3) Epstein and Carhart;(4) and Chow(5) to include, respectively, fluid and solid particles; heat conduction; and fluid particles with particle displacement, large compared with the radius of the particles and the effect of the surface tension. Recently, Chu and Chow(6) developed a theory including both dispersion and attenuation and showed an excellent agreement with the observed values. There is little work done on high particle concentration. Chu(7) obtained a theory from thermodynamic point of view. Nesterov(8) constructed a model and studied the case where viscous effect is predominant. Finally, Byzova and Nesterov(9) proposed a theory which is valid if the mechanical equilibrium exists between the phases. None of the above theories uses equations governing two-phase flows. In this study, the equations governing the motion of a two-phase medium are derived from a continuum theory. The motion of the fluid is governed by a system of integro-differential equations. This theory is used to obtain the dispersion and the attenuation of the sound waves, with special attention given to high particle concentration by considering viscous interaction between the particles and the surrounding medium. The law of the interaction was obtained by a schematic model.

Formulation of the Problem

The equations governing the motion of a multicomponent fluid-particle are, respectively, conservation of mass, momentum, and energy.
Dispersed and Attenuation of Sound in a Highly Concentrated Suspension

\[ \frac{\partial}{\partial t} \rho_i \mathbf{v}_i + \nabla \cdot \rho_i \mathbf{v}_i \mathbf{v}_i = 0 \]  
(1)

\[ \frac{\partial}{\partial t} \Sigma \rho_i \mathbf{v}_i + \nabla \cdot \rho_i \mathbf{v}_i \mathbf{v}_i = \Sigma \mathbf{v} \cdot \mathbf{T} + \rho_i b_i \]  
(2)

\[ \frac{\partial}{\partial t} \left[ \rho_i \mathbf{v}_i \left( u_i + \frac{1}{2} \mathbf{v}_i^2 \right) \right] + \nabla \cdot \rho_i \mathbf{v}_i \left( u_i + \frac{1}{2} \mathbf{v}_i^2 \right) = \nabla \cdot \Sigma \mathbf{v}_i + \rho_i b_i \mathbf{v}_i - \nabla \cdot \mathbf{q} \]  
(3)

\[ \rho_i \] is the mass of the ith specie per unit volume of the mixture; \( \mathbf{v}_i \) is the velocity of the ith specie; \( \Sigma \mathbf{T} \) = stress vector, the average value of a component of the momentum flux on the microscopic scale; \( b_i \) = body force per unit mass of the ith specie; \( u_i \) = internal energy of the ith specie per unit volume of the mixture; \( \mathbf{q} \) = heat flux.

A. The Equation of the Motion of the Fluid. Let us consider the mixture is composed of a gas and the particles of one specie, and is chemically nonreacting. Also, we shall assume that the flow field is in thermal equilibrium. Within the framework of small perturbation and neglecting the stress contribution due to the particles and shear stress due to the gas, the equations governing the motion of the gaseous phase are:

\[ \frac{\partial \rho}{\partial t} + \rho \nabla \cdot \mathbf{v} = 0 \]  
(4)

\[ \rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = \mathbf{F} \]  
(5)

where \( \mathbf{F} \) is the force exerted upon the gaseous phase by the particles per unit volume of the mixture. In the absence of the particles, \( \mathbf{F} \) is equal to zero. The above equations with thermal equation of state \( p = p(\rho, T) \) form a complete system of four equations governing four unknowns. For a fluid with suspension, \( \mathbf{F} \) is dependent upon the state of the flow field surrounding the particles. Finally, the assumption of small perturbation implies that the flow field surrounding a particle can be Fourier decomposed into an infinite number of harmonic oscillations of type \( e^{-i\omega t} \). Consequently, if the force between the particle and the surrounding fluid subjected to a harmonic oscillation are known, \( \mathbf{F} \) may be computed from convolution integral of the type

\[ \mathbf{F} = n_p \mathbf{f}, \quad \mathbf{f} = \int_0^t \mathbf{v}(x, \tau) g(t - \tau) \, d\tau \]  
(6)

where \( n_p \) is the number density of the particles in the undisturbed mixture. Our problem, then, reduces to an analysis of the interaction of a harmonic wave train with a single particle from which \( g(t) \) may be computed.

B. Force Interaction between Particles and Fluid. Here, we shall attempt to obtain the force interaction between the phases without invoking phenomenological laws. In general, it is not simple. Here we shall construct a simplified model and obtain the force interaction between the fluid and particles. Let us isolate one of the particles in the flow field and assume it oscillates at a velocity with respect to the fluid. We shall obtain the force exerted upon the oscillating particle, and then obtain the force on the particle set into motion by the acoustic waves. We shall conceptually construct a layer of fluid surrounding and toward the particle. There will be no flow across the surface of the fluid layer and we shall assume the
dispersion and attenuation of sound in a highly concentrated suspension

surface boundary of the fluid layer to be nonviscous. The form of the outside surface of the shell, in general, is very complex. We shall replace the complicated outside shell structure by a simple one, in the form of a spherical liquid layer. Mathematically, the problem is formulated as follows. For an incompressible and Newtonian fluid and the amplitude of the oscillatory motion smaller than the size of the particle, the equations governing the fluid inside the concentric spheres in a coordinate system moving with the inner sphere are:

\[ \nabla \cdot \mathbf{v} = 0 \]  
\[ \frac{\partial \mathbf{v}}{\partial t} = \frac{\nabla \mathbf{p}}{\rho} + \nabla^2 \mathbf{v} \]

The boundary conditions are: \( \mathbf{v} = \mathbf{v}_p \) at \( r = r_1 \), and \( \mathbf{v} = 0 \), and \( \mathbf{t} = \mathbf{0} \) at \( r = r_2 \).

\( \mathbf{t}_0 \) denotes the shear stress. The solution of the equations satisfying the boundary condition are:

\[ \mathbf{v} = - \mathbf{v} + \mathbf{v}_p, \quad \phi = (a_i + b_i \frac{1}{r^2}) \cos \theta, \quad A = [c_i j_i(kr) + d_i h_i(kr)] \sin \theta, \]

\[ p = -\omega^2 \mathbf{p}_p + \mathbf{p}_o, \quad k = (1 + i)(\omega/2v)^2, \quad A = A_j \]

(9)

where \( j_i \) and \( h_i \) are, respectively, spherical Bessel and Hankel functions of first order. The constants \( a_i, b_i, c_i \) and \( d_i \) are to be determined from the boundary conditions. The force exerted upon the particle by the fluid is

\[ \mathbf{f}_p = \int (\pi \mathbf{rr} \cos \theta - \pi \mathbf{t} \sin \theta) \, dA \]

(10)

where

\[ \mathbf{t}_1 = \frac{1}{2}, \quad \mathbf{t}_2 = \frac{1}{2}(1 - 3h_i(kr)^2) \quad \text{and} \quad \mathbf{t}_3 = \frac{3}{2}h_i(kr) \]

(11)

If the particle is set into motion by the fluid, \( \mathbf{v}_p \) is represented by \( \mathbf{v} - \mathbf{v}_c \), in Eq. (10), and the equation of motion of the particle is

\[ m_p \frac{\partial \mathbf{v}_p}{\partial t} = (\mathbf{t}_1 + i\mathbf{t}_2)(\mathbf{v}_p - \mathbf{v}) + \frac{3\mathbf{v}}{\mathbf{t}} \]

(12)

where \( m_p \) and \( m_f \) are, respectively, mass of the particle and external force produced by the sound field if both the radius and the displacement of the particle are small compared with the wavelength of the incoming waves. Solving for \( \mathbf{v}_p \) from Eq. (11) in terms of \( \mathbf{v}_c \), we obtain the force exerted upon the particle set into motion by the incident acoustic wave.

\[ \mathbf{f}_p = \omega(m_p - m_f) \left( \frac{\mathbf{t}_1}{\mathbf{t}_1} + \frac{1}{\mathbf{t}_2} \mathbf{v}_p + \frac{1}{\mathbf{t}_3} \mathbf{v}_c \right) \]

(13)

where \( G_1 \) and \( G_2 \) are real numbers. The force exerted upon the fluid by the particle at a point \( \mathbf{x} \) is then

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\[ f(x,t) = -\int_{-\infty}^{+\infty} f_{\omega}(x)e^{-i\omega t}d\omega = -\int_{-\infty}^{+\infty} v_c G(\omega)e^{-i\omega t}d\omega = \int_{-\infty}^{t} v(\omega,\tau)g(t-\tau)d\tau \quad (14) \]

**Attenuation and Dispersion of Sound**

Having obtained the expression for \( f \), let us consider a plane sinusoidal sound wave propagating in the x-direction. The system of equations becomes, after eliminating \( p \) from Eq. (15) with the help of the equation of state:

\[
\frac{\partial p}{\partial t} + \rho_0 \frac{\partial u}{\partial x} = 0 \quad (15) \quad \rho_0 \frac{\partial u}{\partial t} + \frac{C_o^2}{\epsilon_f} \frac{\partial p}{\partial x} = n p \int_{-\infty}^{t} u(x,\tau)g(t-\tau)d\tau \quad (16)
\]

where \( \epsilon_f \) is the volume fraction of the fluid and \( C_o \) is the sound velocity of the gaseous phase at thermal equilibrium. For plane sinusoidal disturbances, the dependent variables \( \rho \) and \( u \) take the form \( \exp[i(\kappa x - \omega t)] \), and the above system of equations has a nontrivial solution if and only if \( k \) satisfies the following characteristic equation.

\[
\left( \frac{kC_o}{\omega} \right)^2 = \epsilon_f + \frac{\omega^2}{pC_o} \quad (17)
\]

\( k \) is, in general, complex and its value depends on the nature of the mixture and on the angular frequency. We may write it as \( k = a + ib \) where \( a \) and \( b \) are real quantities and describe respectively the sound dispersion and attenuation in the medium. All the dependent variables will then depend on \( x \) and \( t \) through the factor exp \( [i(\kappa x - \omega t) - bx] \). Consequently, the phase velocity \( V \) is \( V = \omega/a \). If I denotes the sound intensity, then I will vary with \( x \) according to \( I = I_0 e^{-2ax} \). As \( I \) is proportional to the square of the amplitude of fluctuation of the wave, we have \( a = 2b \).

Solving for the phase velocity \( V \) and the attenuation coefficient \( \alpha \), we obtain

\[
\frac{V^2}{a_o^2} = \frac{2}{E + (E^2 + F^2)^{\frac{1}{2}}} \quad (18), \quad \alpha = \frac{\omega}{a_o} \left( \frac{k}{2E^2 + F^2} \right)^{\frac{1}{2}} \quad (19)
\]

where \( E = \epsilon_f - n \frac{C_o}{\rho_o} \omega^2 \), \( F = n \frac{C_1}{\rho_o} \omega^2 \). The expression for \( V \) approaches to Chu's result (7) when \( \omega \to 0 \). Further, for small particle concentration, i.e., \( (\tau_1/\tau_2)^3 \ll 1 \), both \( V \) and \( \alpha \) reduce to the result obtained by Chu and Chow (6) by neglecting the thermal effect. In conclusion, a theory is obtained from which one is enabled to calculate the dispersion and attenuation of sound waves in a highly concentrated suspension where the effects of viscous interaction between phases and between particles are important.

**References**


— J - 84 —
Liquids possessing density anisotropy

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of the Academy of Science of the USSR

The inertial properties of certain inhomogeneous liquids are anisotropic and can be characterized by a density tensor rather than by a scalar density. Let us study the acoustical properties of such a medium assuming that its density tensor $\rho_{ik}$ is known. The equation of motion is

$$\rho_{ik} \ddot{v_k} + \partial p/\partial x_k = 0$$

(1)

where $p$ is the acoustical pressure and $v_k$ is the particle velocity.

The Hooke's law is expressed by an equation of the same form as for isotropic liquids:

$$\rho \ddot{p} + \partial v_k/\partial x_k = 0$$

(2)

where $\rho$ is the liquids compressibility. Eliminating $v_k$ from (1) and (2) we obtain the generalised wave equation

$$\rho \ddot{p} - R_{ij} \partial^2 p/\partial x_i \partial x_j = 0$$

(3)

where $R_{ij}$ is the reciprocal density tensor defined by the equation $R_{ij} \rho_{ik} = \delta_{ik}$. For the harmonic oscillations (3) becomes

$$\omega^2 \rho + R_{ij} \partial^2 p/\partial x_i \partial x_j$$

(4)

This equation has solutions $p = \exp(i\kappa \cdot x)$ representing plane waves travelling in the direction of the propagation vector $\kappa$. The characteristic equation for the latter is
Liquids possessing density anisotropy

\[ \frac{R_{ij}}{\omega^2 \rho} \kappa_i \kappa_j = 1 \]  \hspace{1cm} (5)

Radius vectors of the ellipsoid defined by (5) represent propagation vectors of the plane waves. The corresponding phase velocities \( c = \frac{\omega}{k} \) satisfy the equation

\[ c^2 = \frac{R_{ij}}{\rho} \kappa_i \kappa_j \]  \hspace{1cm} (6)

\( \kappa \) being the modulus and \( \kappa_i = \frac{\kappa_i}{\kappa} \) - the direction cosines of the propagation vector. The equation (6) defines the phase velocity ellipsoid conjugated with the propagation vector ellipsoid (5). Radius vectors of the ellipsoid (6) are equal to the phase velocities of the plane waves propagating in the direction of the normal to the ellipsoid. The principal half-axes of ellipsoids (5) and (6) are

\[ \kappa_1 = \sqrt{\bar{S}_1 \omega^2 \rho}, \kappa_2 = \sqrt{\bar{S}_2 \omega^2 \rho}, \kappa_3 = \sqrt{\bar{S}_3 \omega^2 \rho}; \bar{S}_1 = \frac{1}{\bar{S}_1}, \bar{S}_2 = \frac{1}{\bar{S}_2}, \bar{S}_3 = \frac{1}{\bar{S}_3} \]

respectively, \( \bar{S}_1, \bar{S}_2, \bar{S}_3 \) being the values of \( S_{ik} \) in the direction of principal axes. The particle velocity in an harmonic wave is

\[ v_j = -\frac{1}{i \omega} R_{ij} \frac{\partial \rho}{\partial x_i} \]  \hspace{1cm} (7)

For a plane wave we have

\[ v_j = \frac{\kappa_i}{\omega} R_{ij} \rho \]  \hspace{1cm} (8)

The particle velocity in a plane wave is thus parallel to the radius vector of the ellipsoid (6). Plane waves in a medium possessing an anisotropic density are therefore not longitudinal waves (principal directions excepted).

We proceed now to the determination of the sound field of a point source (for instance a pulsating sphere) with a given volume velocity \( V \). Taking the principal axes of the density tensor as the coordinate axes we obtain from (4)

\[ \omega^2 \rho \nu + \frac{1}{\bar{S}_1} \frac{\partial^2 \rho}{\partial x_1^2} + \frac{1}{\bar{S}_2} \frac{\partial^2 \rho}{\partial x_2^2} + \frac{1}{\bar{S}_3} \frac{\partial^2 \rho}{\partial x_3^2} = 0 \]  \hspace{1cm} (9)

Introducing new variables \( x_1' = \bar{S}_1 x_1, x_2' = \bar{S}_2 x_2, x_3' = \bar{S}_3 x_3 \) we obtain from (9) the equation \( \frac{\partial^2 \rho'}{\partial x_1'^2} + \frac{\partial^2 \rho'}{\partial x_2'^2} + \frac{\partial^2 \rho'}{\partial x_3'^2} = 0 \).

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Liquids possessing density anisotropy

The transformed volume velocity is \( V' = \sqrt{\rho_1 \rho_2 \rho_3} V \). The sound field of the source is therefore \( p = -i \omega V' \exp(i \mathbf{k}' \cdot \mathbf{r}')/4 \pi V' \) where \( \mathbf{r}' = x'_1 x'_2 x'_3 \).

Returning to the old variables we have

\[
p = -i \omega \sqrt{\rho_1 \rho_2 \rho_3} V \exp \left( i \omega \left( \sqrt{\rho_1 \rho_2 \rho_3} \sqrt{x_1^2 + \rho_2 x_2^2 + \rho_3 x_3^2} \right) / 4 \pi \left( \sqrt{\rho_1 x_1^2 + \rho_2 x_2^2 + \rho_3 x_3^2} \right) \right).
\]

Wave fronts of this field coincide with ellipsoids

\[\rho_1 x_1^2 + \rho_2 x_2^2 + \rho_3 x_3^2 = C \omega^2 t\]

which are similar to the phase velocity ellipsoidal. We see that the wave generated by a point source is not spherical. Pressure amplitude is constant along the whole wave front so that the directivity pattern is similar to the wave fronts. The particle velocity components in the near-field zone are

\[
v_x = \frac{\sqrt{\rho_1 \rho_2 \rho_3}}{4 \pi (\rho_1 x_1^2 + \rho_2 x_2^2 + \rho_3 x_3^2)^{3/2}} v_x, \quad v_y = \frac{\sqrt{\rho_1 \rho_2 \rho_3}}{4 \pi (\rho_1 x_1^2 + \rho_2 x_2^2 + \rho_3 x_3^2)^{3/2}} v_y, \quad v_z = \frac{\sqrt{\rho_1 \rho_2 \rho_3}}{4 \pi (\rho_1 x_1^2 + \rho_2 x_2^2 + \rho_3 x_3^2)^{3/2}} v_z.
\]

The velocity is directed along the radius vector and is constant along each wave front. In the far-field zone the particle velocity has the same direction as in a plane wave travelling along the radius vector.

There are certain particularities in the behaviour of waves in the liquids under consideration. For example, the propagation of a plane wave in such a liquid enclosed in a tube is as possible as in an ordinary liquid. However, if the axis of the tube does not coincide with one of the principal axes of \( \phi_{ik} \), the propagation vector is inclined to the tube's axis and the wave travels across the tube. Another example is the Fresnel's problem of the refraction of a plane wave in an ordinary liquid impinging on a plane boundary with an anisotropic liquid. If the boundary does not lie in one of the principal planes of \( \phi_{ik} \), then for some angles of incidence the two waves in the anisotropic liquid satisfying Snell's law will both travel from the boundary or towards the boundary. The explanation of this paradox lies in the fact, that only one of these waves will have its group velocity directed from the boundary; this wave is the refracted one, whatever be its phase velocity direction.
Liquids possessing density anisotropy

In conclusion let us calculate the density tensor for a particular liquid possessing density anisotropy. Such a medium can be realized in a liquid with an immersed rigid grating, or in a liquid suspension of solid particles with a regular orientation. The density tensor of a suspension is calculated in the following way. Let \( \varrho' \) be the density of the liquid and \( \varrho' \) -the density of the solid particles. The macroscopic equation of motion of this micro-inhomogeneous medium is

\[ F_i = \varrho \dot{v}_i + \varepsilon (\varrho' - \varrho) \dot{u}_i \]  
(10)

where \( F_i \) is the force acting on a unit volume of the suspension, and \( \dot{v}_i \) and \( \dot{u}_i \) are the velocities of the medium and of the solid particles respectively. The velocity \( \dot{v}_i \) is determined from the equation

\[ (\varrho' \varepsilon \delta_{ik} + \varrho m_{ik}) u_k = (\varrho \varepsilon \delta_{ik} + \varrho m_{ik}) v_k \]  
(11)

where \( m_{ik} \) is the tensor of the added mass for a solid particle calculated for a unit volume of the suspension. From (11) we find

\[ u_i = [\delta_{ik} - \varepsilon (\varrho' - \varrho) N_{ik}] v_k \]  
(12)

where \( N_{ik} \) is reciprocal to the tensor \( \varrho' \varepsilon \delta_{ik} + \varrho m_{ik} \). (10) and (12) give

\[ F_i = \varrho \dot{v}_i + \varepsilon (\varrho' - \varrho) [\delta_{ik} - \varepsilon (\varrho' - \varrho) N_{ik}] \dot{v}_k = [\delta_{ik} \varepsilon + \varepsilon (\varrho' - \varrho) [\delta_{ik} - \varepsilon (\varrho' - \varrho) N_{ik}]] \dot{v}_k. \]

Therefore the density tensor is

\[ \varrho_{ik} = [(-\varepsilon \varrho + \varepsilon \varrho')] \delta_{ik} - \varepsilon (\varrho' - \varrho)^2 N_{ik} \]  
(13)

The principal axes of the density tensor coincide with the principal axes of \( m_{ik} \). The first term in (13) is the arithmetically averaged density of the suspension. The second term is the dynamical correction; it is always negative, and thus all the components of the density tensor are always smaller, than the averaged value. In this way the inertial mass of the suspension is smaller, than its gravitational mass (this statement is of course valid also for isotropic suspensions with spherical particles). For fixed solid particles (\( \varrho' \rightarrow \infty \)) we have \( \varrho_{ik} = (\varepsilon-1) \varrho \delta_{ik} + \varrho m_{ik} \). For massless particles (\( \varrho' \rightarrow 0 \))

\[ \varrho_{ik} = (\varepsilon-1) \varrho \delta_{ik} - \frac{1}{2} \varrho \delta_{ik} \]  

where \( N_{ik} \) is reciprocal to the tensor \( m_{ik} \).
Absorption and Velocity of Ultrasound in a Critical Mixture of Aniline and Cyclohexane.

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I) Introduction

While the equilibrium properties near the critical point have been studied so far extensively both from the experimental and the theoretical point of view only few works exist on transport properties.\(^{(1)}\)

In this note we report measurement of sound absorption and velocity in the homogeneous phase of an aniline-cyclohexane mixture at the critical concentration.\(^{(2)}\)

Our purpose is to provide sufficiently accurate data near the critical point in order to make possible comparison with existing theories. In this regard our attention is concentrated in the frequency and temperature dependence of sound propagation.

II) Experimental procedure

The absorption has been measured by a pulse method employing a Sperry Ultrasonic Corparator at 2 and 6 mc, and Matec transmitter-receiver combined with a Hewlett-Packard comparison signal generator at 15, 25, 35 and 55 mc. Velocity was measured at 2 and 6 mc. by continuous waves, employing a standard ultrasonic interferometer and measuring the frequency with a Hewlett-Packard digital frequency meter. At the higher frequencies the velocity was measured with a 2-crystal absorption cell, employing the heterodyne
method of Mc Skimin and Mason. For temperature control a Leeds-Northrup 8401 constant-temperature bath was used. For temperature measurement a Pt resistance thermometer of Leeds-Northrup was used in connection with a Cambridge Smith difference bridge.

III) Experimental results

Data are summarized in figures 1) 2) and 3 showing respectively:
1) sound velocity as a function of temperature
2) sound absorption as a function of temperature at 2 Mc
3) sound absorption as a function of frequency at various temperatures.

The precision of the velocity measurement is 0.1%. Within this accuracy there is no evidence of dispersion.

In every case, the accuracy of an absorption measurement depends on the reliability of attenuators. In addition, where a comparison method is employed, it depends on the equal response of the system to the transmitted signal and the comparison signal. In the course of the measurements, we compared results with the Sperry Comparator and the H.P. comparison signal generator at 15 mc; the results were in accord within 1%, which is about the optimum to be expected from the comparison method. At 6 megacycles, only the Sperry comparator could be used, but the response of the system was the same for both the transmitted and comparison signal to within our ability to judge equality of height of signal. At 2 megacycles, however (again with the Sperry comparator) change of gain of the receiver affected the comparison signal somewhat more than the transmitted signal. It is to be noted that the receiver gain was not changed during a 2 mc run; however we felt that there was still the possibility of some error due to the changing signal-height during an absorption measurement.

For this reason, as a further check on the experimental values, we measured the absorption in benzene at 2 and 6 mc. with the Sperry comparator, obtaining, at 25°, the values 950 and 900x10^-17 for \( \frac{a}{E^2} \), with an estimated accuracy of 3%. The 2 mc value
was corrected for diffraction, using the values of Carome, Witting and Fleury for the diffraction loss as a function of $a^2/\lambda$ and path length. Taking all these things into consideration, it seems that the experimental error is of the order of 5% at 2 mc, and somewhat less at the higher frequencies.

We are going into this point because it is essential to establish the bounds of accuracy of the absorption at 2 mc. Extreme precision is not required; but since the 2 mc value greatly exceeds the other values it is essential to know that this large change is real, and not an artifact of the system or of the measurement method. Leeds and Northrup constant temperature both provide a constant temperature to within 0.001°C for several ours. Temperature measurement has been performed with a Leeds and Northrup Pt resistance thermometer and the accuracy was 0.01°C.

IV) Discussion

It has been found possible to fit the results to single-relaxation curves with a relaxation frequency varying from about 6 to 2.5 megacycles as the temperature approaches the critical. This indicates the possibility of interpreting the results as due to a complex specific heat, along the lines of Fixman\(^5\). It does not rule out, however, the possibility of scattering, which was found by Richardson and Brown\(^2\) in an independent measurement in which off-axis radiation was detected.

REFERENCES

2) Previous measurements on this system have been made by Brown and Richardson Phil. Mag. 4, 705 (1959).
FIG. 1
VELOCITY
AT 2 Mc

FIG. 2
ABSORPTION
AT 2 Mc

FIG. 3
$\frac{\alpha}{f^2}$ AS A FUNCTION OF FREQUENCY AT SEVERAL TEMPERATURES
Thermal Relaxation in Methane as affected by Large Concentrations of Oxygen and Nitrogen.

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Introduction

To date, about 200 investigations have been carried out to determine the relaxation time in gas mixtures \(^{(1)}\); but, with a few exceptions, they are all studies of low concentrations of impurities. Large concentrations present major experimental problems, since the height of the dispersion step may decrease considerably with the concentration of the impurity gas. A Hubbard-type high-pressure acoustic interferometer was found suitable to obtain the sound velocity dispersion for mixtures of methane with nitrogen up to 50\% and of methane with oxygen up to 12\%. Higher percentages of \(O_2\) could not be studied because of the danger of explosion.

In the literature, there is no reported contribution of three body collisions contributing to the \(CH_4\) relaxation process, neither is there any phenomenon different from a single relaxation process for the \(CH_4-N_2\) and \(CH_4-O_2\) mixtures because the relaxation effects of pure \(N_2\) and \(O_2\) are known to be in far remote ranges of \((f/p)\). Pure \(N_2\) has a relaxation frequency of 1 cps/atm, at 203°C \(^{(2)}\), pure \(O_2\) of 90 cps/atm, at 50°C, whereas the relaxation frequency of pure methane was found by the author to be approximately 130 kcps/atm, at 52°C. This result for pure methane is puzzling, because independent measurements performed in the same laboratory \(^{(3)}\), on methane purchased from the same distributor, but using a Hubbard low-pressure acoustic interferometer (i.e. 1 atm and below), gave a result of approximately 70 kcps/atm. The methane velocity and wavelength data of the two investigators agree. The factor of two in the relaxation frequency is still unexplained.

There is a reported contribution of a resonance effect in which vibrational energy is exchanged directly between methane and oxygen \(^{(4)}\). This means
Thermal relaxation in methane as affected by $N_2$ and $O_2$.

that $(f/p)_0$ is not linearly shifted in proportion to the concentration of the additive impurity, and hence follows the trace of a conic section (5).

Measurements were made at pressures from 1 atm. to 38 atm., all at constant temperature of 52°C and at the same frequency of 1 Mc. The use of this particular frequency was implicitly suggested by B.T. Kelley (6) who investigated the rotational relaxation in methane and had to make use of a frequency of 2.9 Mc. and of pressures from 2 to 50 cm Hg.

**Relaxation results**

If $N_2$ or $O_2$ be added to $CH_4$ in suitable amounts, the important velocities and relaxation frequencies are listed in the following Table I:

<table>
<thead>
<tr>
<th>Mixture</th>
<th>$(v_\omega)_\text{exp}$</th>
<th>$(v_\omega)_\text{calc}$</th>
<th>$(v_\omega - v_0)_\text{calc}$</th>
<th>$(f/p)_0$</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% $CH_4$</td>
<td>472.8</td>
<td>473.9</td>
<td>7.3</td>
<td>130</td>
<td>6.0%</td>
</tr>
<tr>
<td>10% $N_2$</td>
<td>458.3</td>
<td>458.1</td>
<td>6.5</td>
<td>123</td>
<td>5.4%</td>
</tr>
<tr>
<td>30% $N_2$</td>
<td>432.4</td>
<td>431.2</td>
<td>5.2</td>
<td>114</td>
<td>3.9%</td>
</tr>
<tr>
<td>50% $N_2$</td>
<td>409.8</td>
<td>409.0</td>
<td>3.8</td>
<td>103</td>
<td>4.0%</td>
</tr>
<tr>
<td>12% $O_2$</td>
<td>444.5</td>
<td>449.1</td>
<td>6.4</td>
<td>128</td>
<td>5.2%</td>
</tr>
</tbody>
</table>

The experimental values of $v_{\inf}(p=0)$ were determined by extrapolating the velocities below 3 atm. to zero. The error between the experimental and theoretical value of $v_{\inf}$ might have evolved from minute indeterminations in the concentrations or from variations in temperatures.

The estimated total error limits in determining $(f/p)_0$ for each mixture are indicated in figures (1) and (2). The true relaxation frequency for each concentration should lie somewhere on these bars. It would seem, however, from the way the data points lie on a straight line, that the true errors for $CH_4-N_2$ mixtures are considerably smaller than the error estimates.

In quantitative terms, the data are well fitted by the following equations, where $(f/p)_0$ is in cps/atm and $x$ is the mole fraction of the impurity gas with respect to the total amount of gas present:

1. $(f/p)_0 = 130,000 - (53,900) x$ for $CH_4-N_2$ mixtures
2. $(f/p)_0 = 130,000 - (18,500) x$ for $CH_4-O_2$ mixtures.

From the relation $1/\tau_{\text{mix}} = x_A/\tau_{AA} + x_B/\tau_{AB}$ the value of $1/\tau_{AB}$ was taken to be the 0% $CH_4$ concentration intercept of $1/\tau_{\text{mix}}$. These values are the relaxation times of one molecule of methane in pure nitrogen $(2.4 \times 10^{-6} \text{ sec})$, and in pure oxygen $(1.6 \times 10^{-6} \text{ sec})$, each at standard atmospheric pressure. The error associated with $1/\tau_{AB}$ was the average of the errors of the experimental points.
namely 4.8% for $\tau_{AB}(N_2)$ and 5.6% for $\tau_{AB}(O_2)$. The relaxation results and
the collision numbers $Z_{AA}$ and $Z_{AB}$ for all the data are collected in the
following Table II:

<table>
<thead>
<tr>
<th>Mixture</th>
<th>T (°K)</th>
<th>(10^{-6} sec)</th>
<th>Z</th>
<th>$Z_{AB}/Z_{AA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>325.8</td>
<td>1.39</td>
<td>15300</td>
<td>1</td>
</tr>
<tr>
<td>CH(_4) - N(_2)</td>
<td></td>
<td>325.8</td>
<td>2.38</td>
<td>84290</td>
</tr>
<tr>
<td>CH(_4) - O(_2)</td>
<td></td>
<td>325.8</td>
<td>1.63</td>
<td>57450</td>
</tr>
</tbody>
</table>

Hence it can be seen that $Z_{AA} < Z_{AB}(O_2) < Z_{AB}(N_2)$, from which we can
conclude that both $O_2$ and $N_2$ are less effective in deactivating a methane
molecule than methane colliding with another methane molecule. However,
because of the experimental error of 5.6% in the CH\(_4\) - O\(_2\) mixture (Fig.2),
we can not disprove the finding of Parker\(^7\) that oxygen is just as effective
in deactivating a methane molecule as is methane - methane. In this case,
$Z_{AA}$ would be equal to $Z_{AB}$, and figure (2) should be a horizontal line.

Conclusion

The present dispersion measurements with $N_2$ and $O_2$ as impurities were
quite successful as far as the CH\(_4\) - N\(_2\) mixtures were concerned. There is no
indication of a contribution from three body collisions. Spectroscopic data
indicate that $N_2$ has its lowest excited vibrational level at a characteristic
temperature of 3336°K, while CH\(_4\) has one at 2198°K. There is no reason for
assuming a resonance between CH\(_4\) and $N_2$.

For oxygen the spectroscopic data show an excited vibrational level at
$T^\ast = 2239°K$ which is close to $T^\ast = 2198°K$ of methane. One should expect, (and
could actually postulate, as Schmaus\(^4\) does) that there is a resonant ex-
change of the type CH\(_4\)^\ast + O\(_2\) $\longrightarrow$ CH\(_4\) + O\(_2\)^\ast . The asterisk, in this case,
refers to the resonance of $T^\ast (CH_4)$ and $T^\ast (O_2)$. However, it has been shown by
Magdosky\(^8\) that the predominant specific heat contribution does not evolve
from $T^\ast (CH_4)$ but from $T^\ast (CH_4) = 1881°K$. Since $T^\ast (CH_4)$ is by no means close
to $T^\ast (O_2) = 2239°K$, the assumption of a linear relaxation process for the
CH\(_4\) - O\(_2\) mixtures seems to be valid. So we conclude that the results are
correct, although the danger of explosion prevented further work with oxygen
at concentrations higher than 12%.

—J-95—
Thermal relaxation in methane as affected by $N_2$ and $O_2$

Fig. 1: Relaxation frequency of $CH_4$ vs. mole fraction of $N_2$

$$\frac{f}{p}_0 = 130000 - (53900) x$$

Fig. 2: Relaxation frequency of $CH_4$ vs. mole fraction of $O_2$

$$\frac{f}{p}_0 = 130000 - (18500) x$$

References: