ARCHIVES OF ACOUSTICS
3, 1, 3-15 (1978)

THE APPLICATION OF LONG-TERM ANALYSIS OF THE ZERO-CROSSING OF A SPEECH SIGNAL IN AUTOMATIC SPEAKER IDENTIFICATION

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This paper investigates the possibility of using long-term analysis of the zero-crossings of a speech signal for speaker identification. The applied method of identification is based on an analysis of the signal in measuring windows of a duration which should ensure the stationarity of the statical distributions of the time intervals between successive zero-crossings, in 16 pre-set time channels.

An objective method of defining the minimum length of the measuring window for a selected set of parameters is presented. It is based on the stationarity test and the ergodic theorem for stochastic processes, as is the transformation of the speech signal mentioned above. An experiment in speaker identification for 10 speakers with 10 repetitions for each speaker has been performed. The results obtained, in well exceeding 90% correct identification for 30- and 40 second samples of the speech signal, have confirmed the practicality of the method of zero-crossing analysis for speaker identification.

1. Introduction

The problem of speaker identification on the basis of the analysis of a speech signal still arouses the interest of scientists. The investigations in progress [3, 4, 5, 9, 10] are aimed at using such parameters for voice recognition as would be effective from the viewpoint of the storage of information on an individual, and at the same time being suitable for digital processing without the costly and complicated transformation of the speech signal.

Previous investigations [8] have shown that zero-crossing analysis is a method which can be used for speaker identification. It thus satisfies to some extent the first of the above-mentioned postulates.

In addition this method fully meets the other postulates. Its main advantages, i.e. ease of extraction and subsequent digital processing of a selected set of parameters, have determined that it, primarily, is used for speech analysis and recognition [2, 6].

The purpose of this paper is the investigation and explanation of certain problems that result from the use of the method of the analysis of the zero-

-crossings of a speech signal for speaker identification with the aid of a long-term analysis of this parameter.

Worthy of note is that the speaker identification methods can be divided generally into the methods based on the analysis of a short-term and long-term analysis of a speech signal.

The methods of short-term analysis are based on the individual parameters of the voice obtained from a established text in a time ranging from a fraction of a second for single phonemes, up to several seconds for sentences.

The methods based on long-term analysis are characterized by the fact that during the recognition process use is made of a set of parameters obtained from the speech signal which is of such a duration that the parameters may be considered to be stationary.

Advantages of the long-term methods of analysis are thus their lack of dependence on the text of a statement (i.e. utterance, pronouncement), the elimination of the associated problem of time normalization and also a high probability of correct speaker identification [4]. A real disadvantage, however, is the comparatively long duration of speaker statement necessitated. The problem of determining the minimum length of time for the long-term analysis of a speech signal is of considerable practical importance and constitutes one of the main aims of this paper.

2. The statistical distribution of the time intervals between the zero-crossings of a speech signal

Let $U(t)$ be the time function of a speech signal. If this signal is subjected to some amplification and infinitive peak clipping, then the resulting function $V(t)$ (Fig. 1) can be written in the form

$$V(t) = \text{sign}\ [U(t)]. \tag{1}$$

It can be seen from Fig. 1 that the positions of the zero-crossings after such a transformation of a speech signal remain unchanged under the assumption that the shaper does not introduce any distortion noise which may change the positions of the zeros.

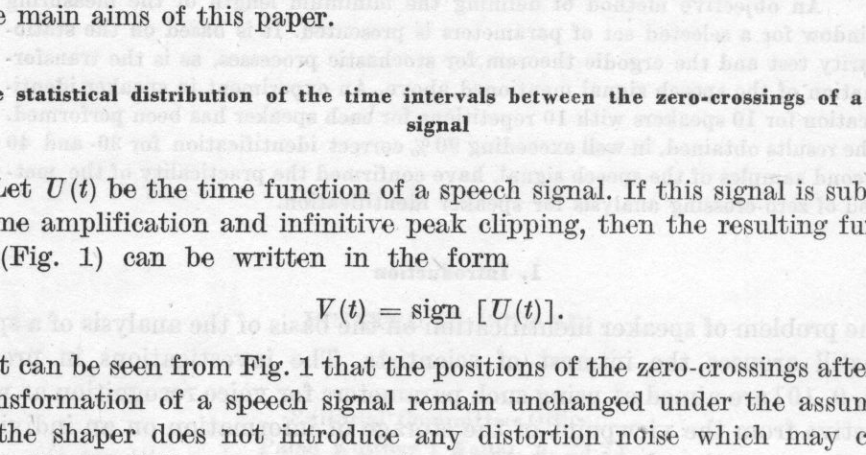

Fig. 1. The pulse shaper (*1* — amplifier, *2* — peak clipping circuit) and the time presentation of signals $U(t)$ and $V(t)$

For the signal $V(t)$ it is possible to define a function $R(t)$ giving the distribution of the time intervals between successive zero-crossings in a given signal segment of duration T_N

$$R(t) = \sum_{j=1}^{J} \delta(t-T_j), \tag{2}$$

where $\delta(x)$ is the Dirac delta function, $j = 1, 2, \ldots, J$ (J is the number of zero-crossings), T_j denotes the interval between a pair j-1 and j of zero-crossings in the segment T_N, with $T_N = \sum_{j=1}^{J} T_j$.

An example of the distribution of the function $R(t)$ is shown in Fig. 2. t_d and t_g are the limiting values of the time intervals for a given signal $V(t)$ in the measuring segment T_N.

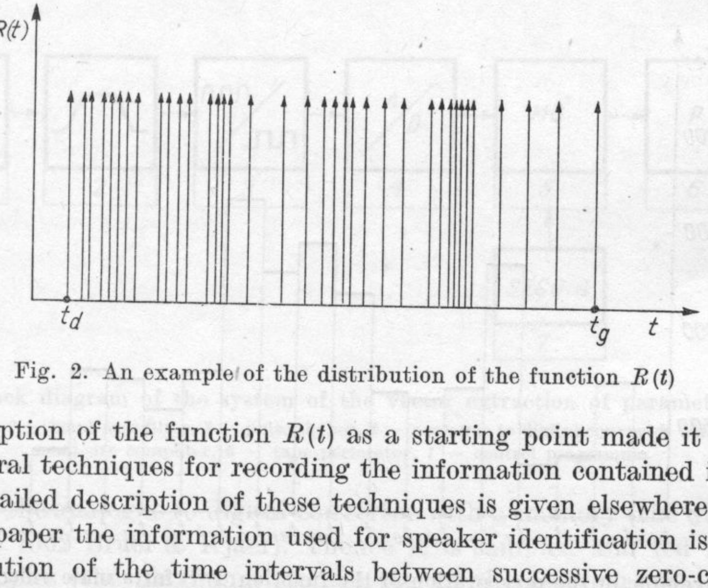

Fig. 2. An example of the distribution of the function $R(t)$

The adoption of the function $R(t)$ as a starting point made it possible to develop several techniques for recording the information contained in a speech signal. A detailed description of these techniques is given elsewhere [6].

In this paper the information used for speaker identification is the statistical distribution of the time intervals between successive zero-crossings in a measuring segment. If in the interval t_d to t_g the $K-1$ of the threshold values are distributed, then one obtains K time intervals called subsequently time channels, or more shortly, parameters. The signal representation mentioned above in the form of the distribution of the zero-crossing in the K time channels will be obtained by summing the number of intervals in suitably chosen ranges.

Let us denote these numbers by

$$y(t_d = t_0, t_1), \quad y(t_1, t_2,), \quad \ldots, \quad y(t_{k-1}, t_k), \quad \ldots, \quad y(t_{K-1}, t_g = t_K). \tag{3}$$

Between these numbers and the function $R(t)$ there the relationship

$$y(t_{k-1}, t_k) = \int_{t_{K-1}}^{t_K} R(t)\, dt. \tag{4}$$

The inclusion of the interval of length T_j in the k-th time channel agrees with the dependence

$$y(t_{k-1}, t_k) = \begin{cases} y(t_{k-1}, t_k)+1 & \text{for } T_j \in (t_{k-1}, t_k), \\ y(t_{k-1}, t_k) & \text{for } T_j \notin (t_{k-1}, t_k). \end{cases} \tag{5}$$

The combined function of the distribution of time intervals in the K time channels can be written in the form

$$Y(t) \overset{\text{def}}{=} \sum_{k=1}^{K} y(t_{k-1}, t_k)[1(t-t_{k-1})-1\ (t-t_k)], \tag{6}$$

where $1(t) = 0$ for $t < 0$ and $1(t) = 1$ for $t \geqslant 0$.

Fig. 3 shows an example of the distribution of time intervals as expressed by the function $Y(t)$.

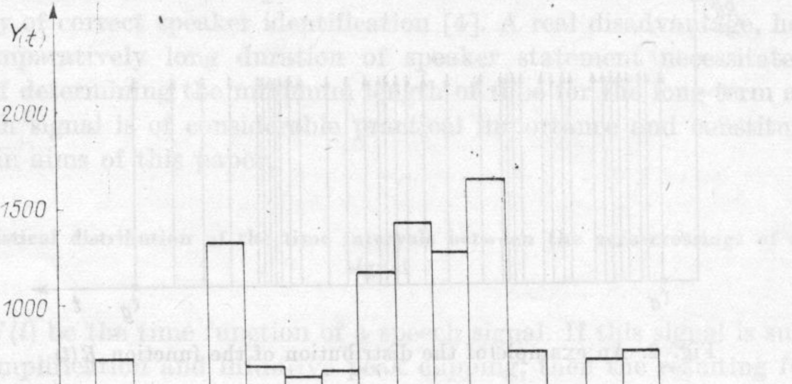

Fig. 3. An example of the presentation of the function $Y(t)$ for a male voice. Time analysis $T^s = 30$ s (the time axis is not graduated)

If the time representation $V(t)$ of duration T_N constitutes pattern (or a time segment of the pattern) of the m-th speaker and of the i-th repetition of the speaker's voice then after having obtained the distribution as a function $Y(t)$ this pattern can be represented in the form of a K-dimensional vector

$$\overrightarrow{y_{m,i}} = \mathrm{col}\{y_{m,i}, y_{m,1,2}, \ldots, y_{m,i,k}, \ldots, y_{m,i,K}\}, \tag{7}$$

where $m = 1, 2, \ldots, M$ (M denotes the number of the speakers), $i = 1, 2, \ldots, I$ (I is the number of repetitions for a speaker and is the same for each of them), $k = 1, 2, \ldots, K$ (K is the number of parameters, being equal to the number of time channels).

3. Phonetic material — the extraction of a set of parameters

The phonetic material for the experiments described in this paper were statements by 10 male speakers in the age range from 20 to 35. The statements of the speakers were recorded in two sessions A and B spaced by a 3 month time interval. In the course of each session for each speaker about 15-20 min. of text were recorded. In session A a newspaper text was recorded, and in session B the text from a popular scientific paper was recorded. The recordings were effected in an audio-monitoring studio. The speech signal was recorded on magnetic tape AN25 by means of microphone MDU26 and tape recorder MP224, produced by ZRK.

The extraction of parameters $\overrightarrow{y_{m,i}}$ was performed as shown in Fig. 4. In this system a signal from the tape recorder at a level of about 40 dB is fed through a band-pass filter (75-5000 Hz and 50 dB/octave) to the pulse shaper whence it is passed to the analogue to digital convertor with a memory (the digital event recorder type 7502 Bruel & Kjaer). Thence it is sampled and fed in portions of 10 240 samples (the maximum storage size of the recorder) for programme processing through a small computer (type 7504 Varian/Bruel & Kjaer). The values of $\overrightarrow{y_{m,i}}$ are read out of the computer onto paper tape (TP).

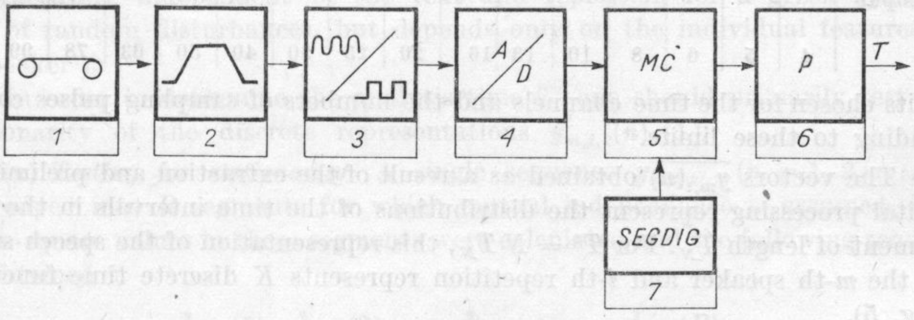

Fig. 4. Block diagram of the system of the vector extraction of parameters $\overrightarrow{y_{m,i}}$
1 — tape recorder, 2 — band-pass filter, 3 — pulse shaper, 4 — analogue to digital convertor with memory, 5 — small-size computer, 6 — tape perforator, 7 — control programme

The calculation of the values of the vectors $\overrightarrow{y_{m,i}}$ is controlled by the program SEGDIG (specially developed for this purpose) which can establish the number K of time channels (parameters) at will, and also their limiting values. The limiting values are given in the form of the numbers of the sampling pulses of the analogue to digital convertor. In the experiments performed, the sampling frequency was $f_p = 20\ 000$ samples/s, permitting the single recording of a signal over a time segment of length $T_N = 0.5$ s. With a view to the need for the extraction of $\overrightarrow{y_{m,i}}$ from time segments that are considerably longer (a subject that will be dealt with in the next section) on automatic system of random readout from the magnetic tape of the signal in a segment of duration $T_N = 0.5$ s was used. The sum of these windows gave the total time of analysis, T^s.

Preliminary results of experimental investigations permitted the determination of the extreme values t_d and t_g for the band 75 to 5000 Hz. This interval was then divided into 16 exponentially divided time channels with an accuracy given by the sampling frequency. Table 1 contains the data concerning the time limits chosen for the time channels and the numbers of sampling pulses corresponding to these limits.

Table 1. Parameters of time channels

K	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
t_{k-1} [ms]	0.15	0.2	0.25	0.3	0.4	0.5	0.65	0.8	1.0	1.25	1.55	0.0	2.5	3.15	3.9	4.95
t_k [ms]	0.2	0.25	0.3	0.4	0.5	0.65	0.8	1.0	1.25	1.55	1.0	2.5	3.15	3.9	4.95	6.22
Bottom	3	4	5	6	8	10	13	16	20	25	30	40	50	63	78	99
Sampled number of impulses																
Top	4	5	6	8	10	13	16	20	25	30	40	50	63	78	99	124

The vectors $\overrightarrow{y_{m,i}(n)}$ obtained as a result of the extraction and preliminary digital processing represent the distributions of the time intervals in the n-th segment of length T_N. For $T^s = N\,T_N$, this representation of the speech signal for the m-th speaker and i-th repetition represents K discrete time functions (Fig. 5).

Fig. 5. Examples of the presentations of the function $y_{m,i,k}(n)$

4. The choice of the time T^s for signal analysis

In many investigations the length of the total analysis time T^s for speaker identification was selected a priori by verifying only the correctness of the choice on the basis of the results of the attempted identification [3, 4, 8]. Such a selection is not, however, an optimal method. The assumption of too long a T^s, i.e. longer than is needed, unnecessarily extends the analysis time, while the selection of too short a segment increases the probability of identification error.

In this paper it is assumed that the distribution of the time intervals between successive zero-crossings of the speech signal measured in the total time of analysis

$$T^s \geqslant \max_{\substack{\wedge \\ m,i,k}} \{T^s_{m,i,k}\}, \tag{8}$$

where $T^s_{m,i,k}$ is the minimum time of the stationarity of $y_{m,i,k}(n)$, $n = 1, 2, \ldots, N$, is practically independent of the text and repetition for a given speaker, and of random disturbances, but depends only on the individual features of a speaker[1]).

In order to determine the analysis time T^s one should primarily test the stationarity of the discrete representations $y_{m,i,k}(n)$ [1].

(a) *Testing for stationarity.* A single sequence $y_{m,i,k(n)}$ $(n = 1, 2, \ldots, N)$ is grouped into R segments for which mutual independence is assumed. The mean-square values in these segments were calculated and the following sequence obtained

$$y^2_{m,i,k}(1), y^2_{m,i,k}(2), \ldots, y^2_{m,i,k}(r), \ldots, y^2_{m,i,k}(R). \tag{9}$$

Then the median of the mean-square values was calcultated and the sequence (9) examined for the presence of the basic trend.

If the hypothesis concerning stationarity holds true, then changes in the sequence (9) will be of a random nature and will exhibit no trend.

To verify the stationarity a non-parametric test was performed at a level of significance of $\alpha = 0.05$. For the tested signals $y_{m,i,k}(n)$ it has been assumed that $T_N = 0.5$ s, $N = 100$ and $R = 20$. From the table containing the value of quantities i_p of the order $1-\alpha$ of the distribution of the number of series for the sequence $T = 2\ p = 20$ observations $i_{p,1-\alpha} = 6$ and $i_{p,\alpha} = 15$ [1] were read off. This series is the sequence of the values exceeding the median or possessing the values smaller than it which follows or precedes the other sequence.

For the assumption of the hypothesis of stationarity it is sufficient that

$$i_{p,1-\alpha} < i_{se} < i_{p,\alpha}. \tag{10}$$

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(1) Refers to the independence, at a certain level of significance, at recording sessions not too distant in time.

In Table 2 examples of the values of the median for each time channel and a number of series for one voice are presented.

In a test carried out for two randomly selected repetitions and for each m and k the hypothesis of stationarity was confirmed.

Table 2. The value of the median and numbers of the series i_{se} for the stationarity test

k	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Median	250	39	70	300	195	183	58	217	320	300	405	870	590	450	372	19
i_{se}	7	9	7	11	9	13	9	9	12	14	14	10	11	11	8	11

(b) *Definition of* $T^s_{m,i,k}$. In a comparatively simple manner it is possible to define $T^s_{m,i,k}$ for a random stationary ergodic signal. The necessary and sufficient condition of ergodicity (in a broad sense) of a stationary random signal, such as $y_{m,i,k}(n)$, is that [1]

$$\frac{1}{S_{m,i,k}} \sum_{l=1}^{S_{m,i,k}} |C^{yy}_{m,i,k}(l)| \to 0 \quad \text{for } S_{m,i,k} \to \infty, \tag{11}$$

where $l = 1, 2, \ldots, S_{m,i,k}$, and $C^{yy}_{m,i,k}(l)$ is the autocovariance function (see Figs. 6 and 7).

For practical application formula (11) can be re-written in the form

$$\frac{1}{S_{m,i,k}} \sum_{l=1}^{S_{m,i,k}} |C^{yy}_{m,i,k}(l)| \leqslant \delta C^{yy}_{m,i,k}(0), \tag{12}$$

where δ denotes the assumed coefficient of deviation from the value $C^{yy}_{m,i,k}$ (0).

The fulfilment of condition (11) is sufficient for the ergodicity (in a broad sense) of the process $y_{m,i,k}(n)$ and confirms the hypothesis with a level of confidence dependent on the value of the coefficient δ, that is accepted.

Since no experiment can be optionally long, the fulfilment of condition (12) permits definition of the number of samples $S_{m,i,k}$ for practical purposes. This enables the calculation of a minimum time $T^s_{m,i,k}$:

$$T^s_{m,i,k} = S_{m,i,k} T_N. \tag{13}$$

Fig. 6 shows the network of operations of the algorithm PESP for calculating $S_{m,i,k}$ while Fig. 7 gives an example of a discrete autocovariance function.

Table 3 contains maximum values $T^s_{m,i,k}$, selected according to formula (8) from the population of 10 speakers, with 3 repetitions for each speaker and with 16 time channels.

It should be noted that the maximum value, $T^s_{m,i,k}$, exhibits a considerable variation with the different channels. It is highest for channels 12, 13, 14, i.e. the ones corresponding to smaller frequencies.

Fig. 6. The flow-chart of the algorithm PESP

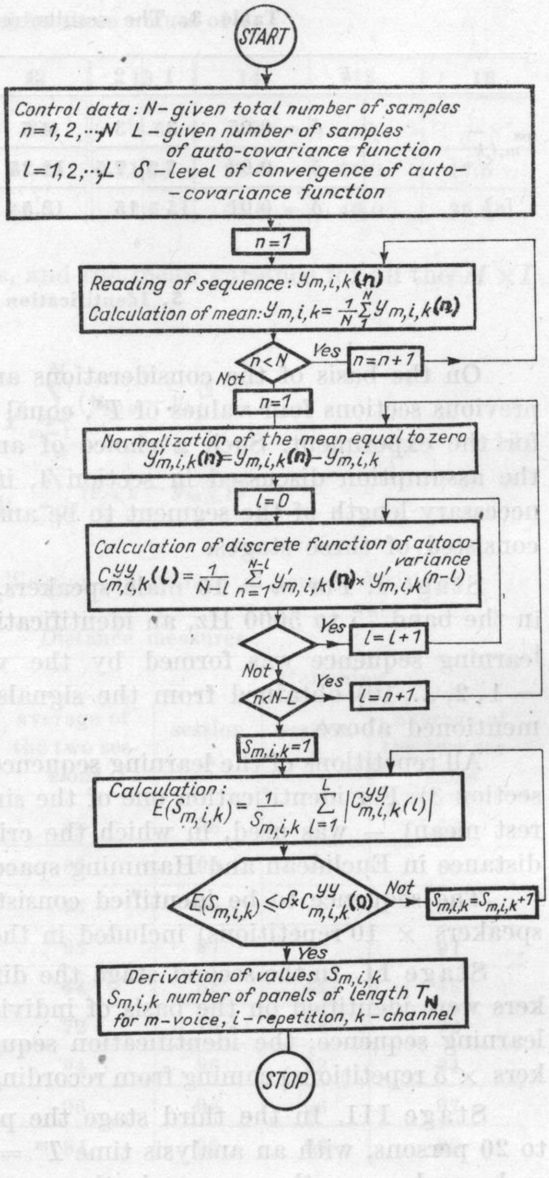

Fig. 7. An example of the presentation of the discrete autocovariance function

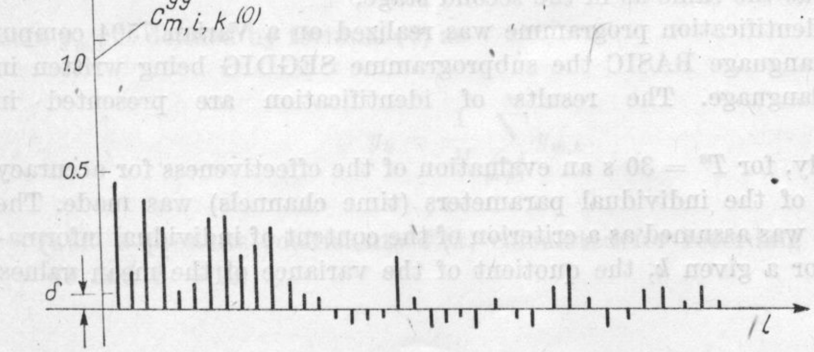

Table 3. The results results of measurements max $\{T^s_{m,i,k}\}$ for

	k	1	2	3	4	5	6	7
$T^s_{m,i,k}$	$\delta = 0.05$	3	3	4.5	6	6	5.5	5
	$\delta = 0.02$	7.5	7.5	11.25	15	15	13.75	12.5
[s]	$\delta = 0.01$	15	15	12.5	30	30	27.5	25.0

5. Identification experiment

On the basis of the considerations and measurement results presented in previous sections four values of T^s, equal to 10, 20, 30 and 40 s, were selected for the experiment. Such a choice of analysis times was intended to check the assumption discussed in section 4, in order to practically determine the necessary length of the segment to be analyzed. The identification experiment consisted of three stages.

Stage I. For $m = 10$ male speakers, $I = 10$ repetitions and for a signal in the band 75 to 5000 Hz, an identification test was carried out in which the learning sequence was formed by the vectors $\overrightarrow{y_{m,i}}$ $(m = 1, 2, \ldots, 10,\ i = 1, 2, \ldots, 10)$ obtained from the signals $V(t)$ for the 4 durations of signal mentioned above.

All repetitions of the learning sequence came from recording session A (see section 3). For identification one of the simplest heuristic algorithms NM (nearest mean) – was used, in which the criterion of decision was the minimum distance in Euclidean and Hamming space [4, 5].

The sequence to be identified consisted of 100 individual statements (10 speakers × 10 repetitions) included in the learning sequence.

Stage II. In the second stage the difference consisted only in that speakers were identified on the basis of individual statements, not included in the learning sequence, the identification sequences being 50 statements (10 speakers × 5 repetitions) coming from recording sessions A and B.

Stage III. In the third stage the population of speakers was increased to 20 persons, with an analysis time $T^s = 40$ s. The number of statements for each speaker was the same as in the second stage.

The NM identification programme was realized on a Varian 7504 computer using the language BASIC the subprogramme SEGDIG being written in the internal language. The results of identification are presented in Table 4.

Additionally, for $T^s = 30$ s an evaluation of the effectiveness for accuracy of recognition, of the individual parameters (time channels) was made. The coefficient $F(k)$ was assumed as a criterion of the content of individual information. $F(k)$ is, for a given k, the quotient of the variance of the mean values

$N = 100, L = 25, f_p = 20\,000$ samples/s and for three values of δ

8	9	10	11	12	13	14	15	16
5.5	7	6.5	7	8.5	8.5	9	8	–
13.75	17.5	16.25	17.5	21.25	21.25	22.5	10.0	17.5
27.5	35.0	32.5	35.0	42.5	42.5	45.0	40.0	35.0

obtained for the individual M speakers, and the mean variance for all the $M\times I$ voices and as given by the formula

$$F(k) = \frac{\dfrac{I}{M-1}\displaystyle\sum_{m=1}^{M}(y_{m,k}-y_k)^2}{\dfrac{I}{(I-1)M}\displaystyle\sum_{m=1}^{M}(y_{m,k}-y_{m,i,k})^2}, \tag{14}$$

Table 4. The results of speaker identification (in percent of correct decisions)

Stage	Number of speakers		Distance measures					
			Euclidean			Hamming		
			session A	session B	average of the two sessions	session A	session B	average of the two sessions
		$T^s = 10$ s	60	–	60	58	–	58
I	10	$T^s = 20$ s	89	–	89	90	–	90
		$T^s = 30$ s	97	–	97	96	–	96
		$T^s = 40$ s	98	–	98	97	–	97
II	10	$T^s = 10$ s	48	40	44	52	44	48
		$T^s = 20$ s	76	68	72	76	68	72
		$T^s = 30$ s	96	92	94	96	92	94
III	20	$T^s = 40$ s	96	96	96	98	96	97
		$T^s = 40$ s	88	80	84	92	86	89

where $y_{m,k}$ is defined by formula (7) as

$$y_k = \frac{1}{M}\sum_{m=1}^{M} y_{m,k}.$$

Table 5 presents coefficients $F(k)$ calculated for recording session A for $M = 10$ and $I = 10$.

It can be seen from Table 5 that the differences in the values of $F(k)$ are not too high and this gives evidence, to some extent, of an even distribution of individual information in selected time channels.

Table 5. The values of ability coefficients of parameters k

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$F(k)$	47.3	54.8	112.1	68.0	34.2	28.3	35.0	40.3	24.9	30.6	18.7	36.0	60.4	25.2	43.3	91.9

6. Discussion of results and conclusions

The results obtained of the identification (Table 4), although concerning not too numerous a population of speakers, confirm practicability of long-term analysis of the zero-crossings of a speech signal as a method for speaker identification. Especially promising are the results obtained for analysis times of 30 and 40 s which give considerably better than 90 % correct identification for $M = 10$, and are comparable to the results of other tests which use much more complicated methods.

An increased population of speakers ($M = 20$) brought about some decrease in the probability of correct identification.

Comparison of the results of identification achieved for various lengths of analysis times permits formulation of the thesis that 30 to 40 s of continuous speech signal from a newspaper text cam be accepted as the minimum time of long-term analysis for the calculation of an eventual distribution of time intervals between successive zero-crossings to be used for speaker identification.

In the case of essential differences from the number of time channels assumed in this paper, and the method of their division, differences from the required stated values $T^s = 30\text{-}40$ s may arise.

Comparing the values given in Table 3 with those in Table 4 a practical conclusion can be drawn that to determine the lengths of the time for analysis according to the method described in section 4 it is necessary to accept $\delta \leqslant 0.02$. If the condition for the stationarity of the distribution of time intervals is satisfied then there should be no essential difference in the results of identification of a particular sequence and whether or not it forms part of the learning sequence.

The results of Table 4 are in agreement with this theorem although to some extent the effect of the time lapse between recording sessions A and B can be seen. This is obvious because the individual features of the voice are not constant and change with time.

For a more comprehensive estimation of the practicality of the method of speaker identification presented consideration should be given to the restrictions assumed by the authors:

1. The experiment was carried out in laboratory conditions and thus the results of identification are independent of the influence of the technical conditions of the recording [7].

2. The extraction of parameters was performed over a frequency band of speech signal from 75 to 5000 Hz. Neither the number of the channels nor the limit of the time channels were optimized, an exponential division within the interval t_d to t_g being assumed a priori.

3. The experiment was carried out with the cooperation of the speakers, i.e. the speakers did not try during the recordings to change the manner of their pronunciation or to imitate the voices of other speakers.

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Received on 25th May 1977

ARCHIVES OF ACOUSTICS
3, 1, 17-34 (1978)

GENERALIZED MODEL OF AN AXIAL DYNAMIC GENERATOR*

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This paper present a model of the theoretical acoustic system of a dynamic axial generator with a horn and pressure chamber common to all channels of the stator. The model has been developed on the basis of electroacoustic analogies. This permits formulation of the wave phenomena encountered in the acoustic system of the generator.

Experimental investigations have shown that the model is correct within the range of conditions assumed during its formation.

Postulates have also been formulated which, when satisfied, will permit the optimal working of the generator over a wider frequency range.

1. Introduction

The development of experimental investigations in the non-linear acoustics of gas media still faces difficulties resulting from the lack of satisfactorily efficient and stable sound sources of high acoustic power. Such a situation also limits the use on an industrial scale of the acoustic coagulation of aerosols and of other ultrasonic technology. This particularly applies to the so-called "flow generators". The main reason for their limited use is their comparatively low acoustic efficiency and thus resulting high operational costs. Another essential reason is the lack of a complete theoretical formulation of the phenomena found within the acoustic system of the generator in the process of transforming the energy of the compressed air into acoustic energy. Thus it is impossible to design a generator of given acoustic parameters and recourse has to be made to the duplication of certainly non-optimal solutions obtained by way of experiment.

Much progress has recently been made in the investigation of static generators in terms of the explanation of their mechanism of operation [7].

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* The paper is written under the supervision of prof. Roman Wyrzykowski.

Dynamic generators may claim a more advanced theoretical description. However, they require further studies, both theoretical and experimental, the aim of which is the description of the generator's properties over the full range of its working conditions.

Jones [4], Allen and Watters [2, 3] and Wyrzykowski [13, 14] have developed a theoretical foundation for the operation of a dynamic generator. A physical model of the dynamic generator developed by them, in view of the accepted simplifying assumptions, should be in agreement with experiment over a range of comparatively low frequencies for the sound wave produced by the generator, i.e. up to several hundred of Hz. This has been confirmed by experiment both by Jones, and by Allen and Watters. Leśniak, while making measurements of the acoustic parameters of the siren KRW [14] observed a sudden drop in the sound power of this generator at higher frequencies, which until now is not explained.

2. The electrical equivalent diagram of the generator and its mathematical description

The acoustic system of a dynamic axial generator (Fig. 1) consists of a pressure chamber, *1*, of which one wall is a flat stator, *2*, with passages arranged evenly on the circumference. The stator passages enter into a chain-type horn of annular cross-section, *3*. In the chamber in front the stator there is a flat rotor, *4*, of small thickness and with holes corresponding to the passages in

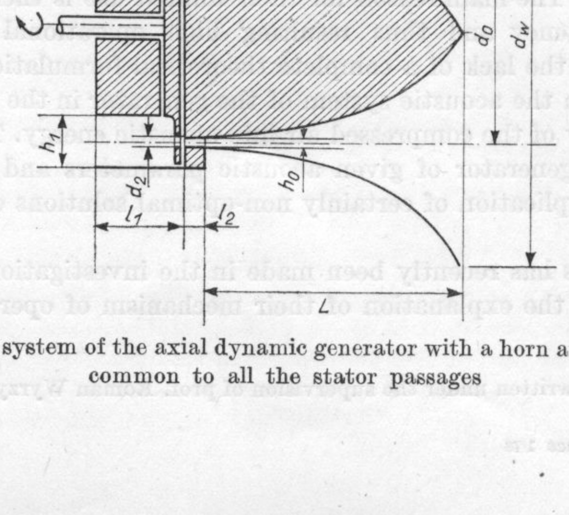

Fig. 1. The acoustic system of the axial dynamic generator with a horn and pressure chamber common to all the stator passages

the stator. The formation of a sound wave takes place in the elementary functional unit of the acoustic system of the generator, composed of the pressure chamber, the hole arrangement of the rotor and stator, the stator passage, and the horn. The number of such units in the acoustic system of the generator ranges from a few to several hundred. They are usually identical, with the pressure chamber and the horn being common to all stator passages.

Compressed air is forced into the pressure chamber in such a quantity that the thermodynamic parameters of the air in the chamber should not undergo any changes caused by the escape of air from the chamber (via the passages and the horn) into the atmosphere. The mass air flow in the acoustic system of the generator, with the rotor stopped, can be described [8] by the relationship

$$M = \alpha \varepsilon S_2 \sqrt{2\varrho_1 \Delta P}, \tag{1}$$

where

$$\alpha = \frac{1}{\sqrt{1-m^2}}$$

is the flow ratio, and

$$\varepsilon = \left[r^{2/\varkappa} \frac{\varkappa}{\varkappa - 1} \, \frac{1 - r^{(\varkappa-1)/\varkappa}}{1-r} \, \frac{1-m^2}{1-m^2 r^{2/\varkappa}} \right]^{1/2}$$

is the expansion coefficient for isentropic air flow out of the pressure chamber, with

$$\Delta P = P_1 - P_2, \quad r = P_2/P_1, \quad m = S_2/S_1.$$

For sufficiently small values (when compared with unity) of m ratio of the cross-sectional area of the stator passage S_2 to the surface of the pressure chamber S_1, and of the pressure differences ΔP of the air in the pressure chamber, P_1, and in the stator passage P_2 (i.e. smaller than $0.2 \times 10^5\ \mathrm{N/m^2}$ Fig. 2) then $\alpha = \varepsilon = 1$ [2, 4, 13] can be accepted in expression (1).

When revolving the rotor periodically opens and closes the inlet hole of the stator passage, so that the active surface for air flow is a periodic function of times $S(t)$. The range of variation of this function is from zero to S_m, with S_m being the area of the wholly open stator passage. The mass air flow thus contains, in addition to the constant component M_0, a component varying with time $M(t)$:

$$M = M_0 + M(t). \tag{2}$$

The latter causes the dependence of the acoustic impedance Z, in the inlet hole of the stator passage, on the acoustic pressure $p(t)$. The pressure drop ΔP now equals

$$\Delta P' = P_1 - [P_2 + p(t)] = \Delta P - p(t), \tag{3}$$

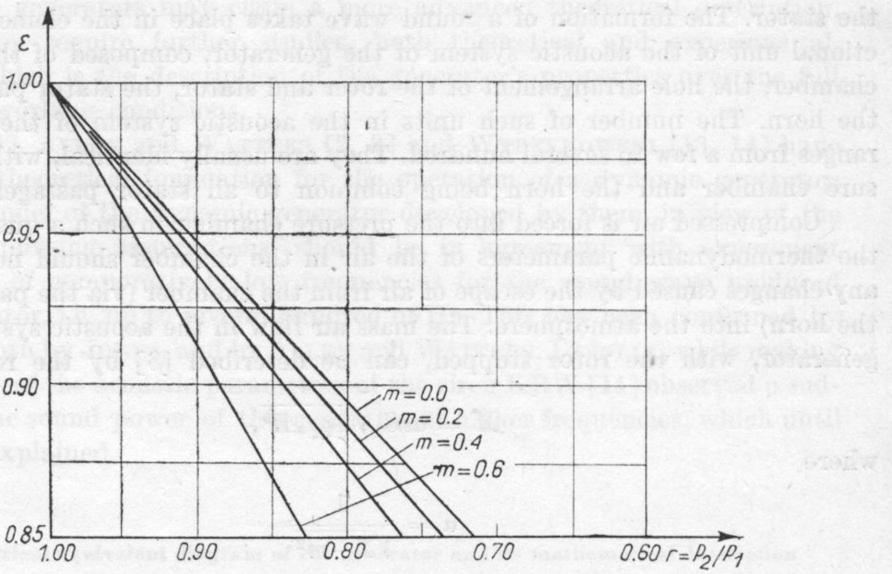

Fig. 2. The relation between the expansion coefficient and the quantities r and m

According to (1), (2) and (3) we thus have

$$S(t) = \frac{M_0 + M(t)}{\sqrt{2\varrho_1[\Delta P - p(t)]}}. \tag{4}$$

In the acoustic impedance Z of the inlet hole of the stator passage we can distinguish its two components as the output impedances:

(i) of the pressure chamber

$$Z_1 = \frac{p_1}{V_1} = X_1 + jY_1, \tag{5}$$

(ii) of the stator passage complete with horn

$$Z_2 = \frac{p_2}{V_2} = X_2 + jY_2, \tag{6}$$

where p_1, p_2 and V_1, V_2 are the root mean square values of the acoustic pressure and the volume velocity of the air at the inlet, of the pressure chamber (for index 1) and of the stator passage (for index 2).

For convenience and generalization we shall in future consider the pressure chamber and the stator, including the horn, as acoustic four-terminal networks the input impedances of which are respectively Z_1 and Z_2. Let us assume that $Z = Z_1 + Z_2$. This thus requires a connection in series of the inputs of these four-terminal networks. An external source of compressed air maintains the upper terminals of the four-terminal network, which represents the pressure chamber, under a constant (in time) pressure P_1. The lower terminals of this four-terminal network are under ambient pressure P_0. Assuming that the only loss of energy of the wave propagating in both four-terminal networks is the loss connected with its outward radiation, which for obvious reasons is equal to zero at zero frequency, it can be accepted that:

(i) the values of the constant component of the air pressure in the pressure chamber P_1 and in the stator passage P_2 do not depend on the position in the air flow path of air of these elements,

(ii) the constant component of the air pressure in the stator passage P_2 is equal to the ambient pressure P_0.

The inlet hole arrangement of the stator passage and of the revolving rotor can be looked upon as the periodically variable (in time) flow resistance, G, the value of which varies between the minimum value when the inlet hole of the stator passages is wholly opened, and infinit when the hole is completely closed.

Figure 3 represents the equivalent electrical circuit diagram of the acoustic system of a dynamic acoustic generator with a horn and pressure chamber common to all the passages.

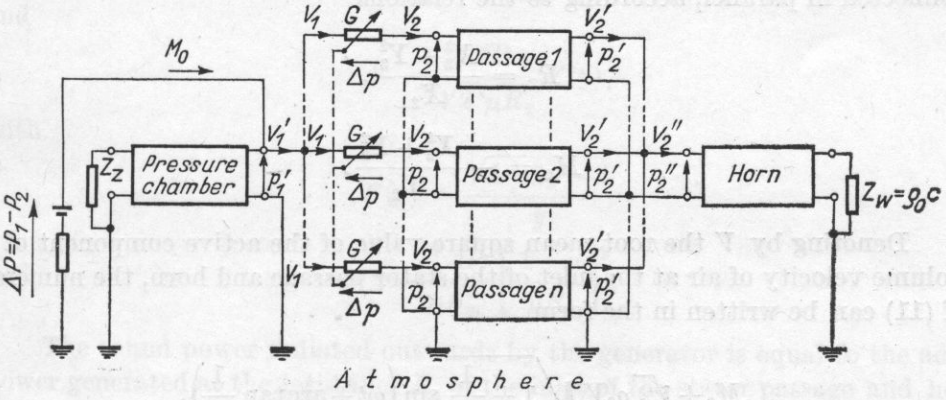

Fig. 3. Electric equivalent circuit of the axial dynamic generator

Let us assume that as a result of the modulating action of the flow resistance G, the instantaneous values of the variable component of the mass air flow, and of the acoustic pressure in the inlet holes of the stator passage are given by the formulae

$$M(t) = M_a \cos \omega t, \tag{7}$$

$$p(t) = p_a \cos \omega t, \tag{8}$$

M_a and p_a being the complex amplitudes of the above-mentioned quantities.

Taking advantage of the equation for the continuity of mass air flow ($V_1 \varrho_1 = V_2 \varrho_2$), from Fig. 3 we can write

$$M_a = \sqrt{2}\,\varrho_2 V_2 = \sqrt{2}\,\varrho_2 \frac{p_2}{Z_2}, \tag{9}$$

$$p_a = \sqrt{2}\,(p_1 + p_2) = \sqrt{2}\,p_2 \left(1 + \frac{\varrho_2}{\varrho_1}\,\frac{Z_1}{Z_2}\right). \tag{10}$$

Substituting (5)-(10) into (4) we obtain

$$S(t) = \frac{M_0 + \sqrt{2}\,\varrho_2 p_2 \left[\dfrac{X_2}{X_2^2+Y_2^2}\cos\omega t - \dfrac{Y_2}{X_2^2+Y_2^2}\sin\omega t\right]}{\sqrt{2\varrho_1 \left\{\Delta P - \sqrt{2}\,p_2 \left[\left(1+\dfrac{\varrho_2}{\varrho_1}\,\dfrac{X_1X_2+Y_1Y_2}{X_2^2+Y_2^2}\right)\cos\omega t + \dfrac{\varrho_2}{\varrho_1}\,\dfrac{X_2Y_1-X_1Y_2}{X_2^2+Y_2^2}\sin\omega t\right]\right\}}}. \tag{11}$$

For convenience in further calculations we shall make a transformation of the components of the combined input impedance of the stator passage and horn $Z_2 = X_2 + jY_2$, connected in series, into their equivalent $Z_2 = R_2 + jM_2$, connected in parallel, according to the relations

$$R_2 = \frac{X_2^2+Y_2^2}{X_2}, \tag{12}$$

$$M_2 = \frac{X_2^2+Y_2^2}{Y_2}, \tag{13}$$

Denoting by V the root mean square value of the active component of the volume velocity of air at the inlet of the stator passage and horn, the numerator of (11) can be written in the form

$$M_0 + \sqrt{2}\,\varrho_2 V \sqrt{1+\frac{1}{k_2^2}}\,\sin\left(\omega t + \arctan\frac{1}{k_2}\right), \tag{14}$$

where

$$k_2 = \frac{M_2}{R_2} = -\frac{X_2}{Y_2} \quad \text{and} \quad V = \frac{p_2}{R_2}.$$

The function $S(t)$, according to the previous assumptions, should satisfy the following conditions:

$$S(t)_{\min} = 0, \tag{15}$$

$$S(t)_{\max} = S_m. \tag{16}$$

Thus, according to (11), (14) and (15), we can write

$$\sin\left(\omega t+\arctan\frac{1}{k_2}\right) = -1, \tag{17}$$

$$M_0-\sqrt{2}\,\varrho_2\sqrt{1+\frac{1}{k_2^2}}\;V = 0. \tag{18}$$

Assuming that (16) occurs at $t = 0$, on the basis of (11), we have

$$S_m = \frac{M_0+\sqrt{2}\,\varrho_2 V}{\sqrt{2\varrho_1\left[\Delta P-\sqrt{2}R_2V\left(1+\dfrac{\varrho_2}{\varrho_1}\,\dfrac{X_1X_2+Y_1Y_2}{X_2^2+Y_2^2}\right)\right]}}. \tag{19}$$

Writing

$$\gamma = \sqrt{1+\frac{1}{k_2^2}} = \sqrt{1+\left(\frac{Y_2}{X_2}\right)^2}, \tag{20}$$

$$\mu = 1+\frac{\varrho_2}{\varrho_1}\,\frac{X_1X_2+Y_1Y_2}{X_2^2+Y_2^2}, \tag{21}$$

from (18) and (19) we obtain

$$M_0 = \sqrt{2}\,\varrho_2\gamma V \tag{22}$$

and

$$V = \frac{\Delta P}{\sqrt{2}\,\mu R_2}\,F(y), \tag{23}$$

with

$$F(y) = \frac{\sqrt{1+2y}-1}{y} \tag{24}$$

$$y = \frac{\varrho_2^2\,\Delta P}{\varrho_1 S_m^2}\left[\frac{1+\gamma}{\mu R_2}\right]^2. \tag{25}$$

The sound power radiated outwards by the generator is equal to the active power generated at the resistance R_2 of the inlet of the stator passage and horn:

$$N_a = V^2 R^2. \tag{26}$$

The power to be needed for generation of the acoustic power, will be calculated as a product of the constant component of the mass air flow M_0 (22) and the work performed in the compression of air from a pressure P_2 to a pressure P_1 by means of an adiabatic compressor with a reversible working cycle [8],

$$N = nM_0L_t, \tag{27}$$

where n is the number of the stator passages.

Work of compression

$$L_T = \frac{\varkappa}{\varkappa-1}\,\frac{P_2}{\varrho_2}\left[\left(\frac{P_1}{P_2}\right)^{\varkappa-1/\varkappa} -1\right]. \tag{28}$$

For sufficiently small pressure drops $\varDelta P = P_1 - P_2$, i.e. not higher than 0.2×10^5 N/m^2, in the expansion

$$\left(\frac{P_1}{P_2}\right)^{\varkappa-1/\varkappa} = \left(1+\frac{\varDelta P}{P_2}\right)^{\varkappa-1/\varkappa} = 1+\frac{\varkappa-1}{\varkappa}\,\frac{\varDelta P}{P_2}+\ldots \tag{29}$$

consideration need be given only to two terms. Then

$$L_T = \frac{\varDelta P}{\varrho_2} \tag{30}$$

and the supply power [4, 13]

$$N = nV_0\varDelta P, \tag{31}$$

where $V_0 = M_0/\varrho_2$ is the constant component of the volume air flow in the stator passage. The acoustic efficiency of the generator

$$\eta_a = Na/N. \tag{31a}$$

3. The internal structure of the four-terminal networks

WYRZYKOWSKI [13] has proved that the optimal catenary horn to be used in conjunction with dynamic generators is one whose profile describes the equation

$$S = S_0 \cosh^2 \frac{z}{z_0}, \tag{32}$$

where S is the cross-sectional area of the horn at a distance z from its inlet, S_0 is the area of the horn inlet and z_0 is the opening coefficient.

The horn with a catenary profile and annular cross-section is formed of two rigid surfaces resulting from the rotation about the axis Oz of the two curves described by the equation (Fig. 1)

(i) upper

$$f_g(z) = \frac{1}{2}\left(d_0 + h_0 \cosh \frac{z}{z_0}\right), \tag{33}$$

(ii) lower

$$f_d(z) = \frac{1}{2}\left(d_0 - h_0 \cosh \frac{z}{z_0}\right). \tag{34}$$

The equation of the profile (32) of such a horn takes the form

$$h = h_0 \cosh^2 \frac{z}{z_0}, \tag{35}$$

where $h = f_g(z) - f_d(z)$.

For $z = L$ we have $f_d(z) = 0$ and usually $f_g(z) = r_w$, with r_w being the radius of the horn outlet. From (34) we have

$$z_0 = \frac{L}{\operatorname{arccosh} \dfrac{d_0}{h_0}}. \tag{36}$$

The wave equation [16] of the wave propagating in a catenoidal horn of annular cross-section has so far been solved for the propagation of a tangential wave mode of zero order (i.e. for a plane wave) and this occur above the cut-off frequency [15].

$$f_0 = \frac{c}{2\pi z_0}. \tag{37}$$

The impedance of the horn inlet as regards the range of propagation of the above-mentioned mode when neglecting the wave reflection from the horn outlet, is given by the relation

$$Z_{to} = \frac{\varrho_2 c}{S_0}\left[1 - \left(\frac{f_0}{f}\right)^2\right]^{-1/2}, \tag{38}$$

whereas the transmission coefficient for acoustic pressure takes the form (Fig. 3)

$$K_{pt} = \frac{p_2'''}{p_2''} = \frac{\exp\left[-j\sqrt{\left(\dfrac{f}{f_0}\right)^2 - 1}\,\dfrac{L}{z_0}\right]}{\cosh \dfrac{L}{z_0}}, \tag{39}$$

where p_2'' and p_2''' are the acoustic pressures at the inlet and outlet of the horn, respectively.

It results from those relationships that a catenoidal horn for the propagation range of the tangential wave mode of zero order represents, for the stator passage, a mere resistance load. At the cut-off frequency the impedance of the horn inlet is infinitely great, while below this frequency it has a pure imaginary value [15]. Thus it can be concluded that below the cut-off frequency of the horn the generator should not produce a sound wave. Only an infinitely long horn can exhibit such properties. The assumption of a boundary condition at the horn outlet of finite length for describing the conditions of radiation of the horn outlet implies that for the cut-off frequency the impedance of the horn outlet must assume a finite value while below this frequency it has a real part, but with values considerably smaller than is the case above the limiting frequency [17]. This is in agreement with experiment since the generator does produce a sound wave below the cut-off frequency of the horn.

With increasing frequency the impedance of the horn inlet tends to the asymptotic value

$$Z_{to} = \frac{\varrho_2 c}{S_0}. \tag{40}$$

A drawback of this discussion is the lack of a statement at which frequency range, in a catenoidal horn, the propagation of an exclusively tangential wave mode of zero order is possible. This is tantamount to the lack of a definition of the range of application the argument presented here. The solution of this problem can only be obtained empirically.

The passage of the generator stator represents a length of acoustic wave-guide, loaded at the outlet with the impedance of the horn inlet, which is common for all stator passages. According to Fig. 3 we can write the impedance loading the outlet of each of the stator passages as

$$Z_2' = \frac{p_2'}{V_2'} = \frac{p_2''}{V_2''/n} = nZ_{to}. \tag{41}$$

In practice each stator passage satisfies the condition for plane wave propagation i.e. that the diameter $d_2 < \lambda/2$, where λ is the wavelength. Neglecting loss of the wave energy which is associated with propagation in the passage an is caused by the viscosity and thermal conductivity of the air, and assuming an ideal boundary condition on the walls of the horn, that the normal component of the vibration velocity amplitude of the medium should there be zero, the acoustic properties of the stator passage can be described by the following relations [18]:

(i) the acoustic impedance of the inlet of the stator passage is equal to

$$Z_2 = Z_{02}\frac{Z_2' + jZ_{02}\tan kl_2}{Z_{02} + jZ_2\tan kl_2}; \tag{42}$$

(ii) the transmission coefficient for the acoustic pressure

$$K_{ps} = \frac{p_2'}{p_2} = \frac{1}{\cos kl_2 + j\dfrac{Z_{02}}{Z_2'}\sin kl_2}, \tag{43}$$

where $k = \omega/c$ is the wave number, l_2 is the length of the stator passage, and $Z_{02} = \varrho_2 c/S_2$ is the wave impedance of the passage.

Here it should be noted that above the cut-off frequency of the horn $Z_{02} > Z_2$, implying the occurence of wave reflection at the place of connection of the passage outlet and the horn inlet. For this reason the inlet impedance of the passage Z_2 possesses a non-zero imaginary part and both components are strongly frequency dependent. The maximum values of Z_2 correspond to the quarter-wave resonances of the stator passage, and the minimum values to the half-wave resonances.

The reflection of the wave at the place of the connection of the stator and the horn becomes weaker as the number of passages in the stator increases (41). However, it is not possible to completely eliminate this phenomenon without basic changes in the acoustic system of the generator in the form of individual horns for each stator passage [14]. Although the construction of such a generator is possible in practice, in view of the practical possibility of using only several horns, the attainment of the satisfactorily high sound powers with the generator at higher frequencies remains a problem.

The pressure chamber, usually annular in cross-section is, like the horn also common to all the stator passages. According to Fig. 3 the input impedance of the pressure chamber, loading each of the inlets of the stator passages is equal to

$$Z_1 = \frac{p_1}{V_1} = \frac{p_1'}{V_1'/n} = nZ_{k0}, \tag{44}$$

where Z_{ko} is the input impedance of the pressure chamber.

The pressure chamber of the generator (Fig. 1) can be regarded as a wave-guide with one end closed by a rigid partition. In the frequency range for which the condition for plane wave propagation is satisfied for the pressure chamber, i.e. for $h_1 < \lambda/2$, analogous assumptions have been made to those for the stator passage. Thus the input impedance of the pressure chamber is described [18] by the relation

$$Z_{k0} = -jZ_{01}\operatorname{cotan} kl_1, \tag{45}$$

where l_1 is the length of the chamber, and $Z_{01} = \varrho_1 c/S_1$ is its wave impedance.

In view of the previous assumption $S_1 \gg S_2$, and $Z_{01} \ll Z_{02}$. The resonance properties of the pressure chamber found at the higher frequencies advesely affect the sound power characteristic of the generator. This particularly applies to the anti-resonance frequency of the chamber for which $Z_{k0} = \infty$, and thus $Z_1 = \infty$. For these frequencies the generator does not radiate sound power as results from relations (21) and (23)-(25) with $\mu = \infty$.

In this situation it is necessary to attenuate the free vibrations of the pressure chamber. This is feasible through the use of an intensively absorbing end. This solution has the advantage that it does not change the conditions of flow through the chamber of the constant component of the mass air flow. The input impedance of the pressure chamber of the generator attenuated in this manner, is equal to the wave impedance Z_{01}.

In the range of higher frequencies the impedance Z_1 loading the inlet of the stator passages with the pressure chamber attenuated in this manner can assume its lowest values for various designs of the chamber [1, 2, 4] while m (1) and n (44) are still not too large.

4. Subject of investigations and its characteristics

In order to provide experimental verification of the theoretical arguments measurements have been carried out on the sound power of an axial dynamic generator detailed characteristics have been given previously [10]. Here only the basic dimensions specified in Fig. 1 are repeated: $d_0 = 100$ mm, $d_w = 200$ mm, $h_0 = d_2 = 1.5$ mm, $h_1 \cong 15$mm, $l_1 \cong 30$ mm, $l_2 = 10$ mm, $L = 150$ mm, $n = 50$. From these dimensions the following values for the characteristic frequencies of this generator may be calculated.

(i) the cut-off frequency of the horn $f_0 = 1790$ Hz

(ii) the frequency of the first resonance of the stator passage $f_{rs} = 8600$ Hz,

(iii) the frequency of the first anti-resonance of the pressure chamber $f_{ak} \cong 6000$ Hz.

In view of the rather complicated construction of the pressure chamber of the tested generator, the definition of the third of the above-mentioned frequencies could only be approximate.

In view of the fact that for the tested generator $S_1 \gg S_2$ it has been assumed that except for those frequencies near to the anti-resonance frequencies of the pressure chamber, $\mu = 1$.

5. Method of measurement of the sound power of the generator

The sound power of the generator is defined by the experimentally measured distribution of the root mean square value of the acoustic pressure at a constant distance r_0 from the horn outlet in the far field of the generator, using the relation

$$N_a = \frac{2\pi r_0^2}{\varrho_0 c} \int_0^{\pi/2} p^2(\vartheta) \sin(\vartheta)\, d\vartheta \tag{46}$$

estimated in the calculations by

$$N_a = \frac{1}{\varrho_0 c} \sum_{i=1}^{m} p^2(\vartheta_i)\, \Delta S_i, \tag{47}$$

where $S_i = 2\pi r_0^2 \sin(\vartheta_i)\, \Delta\vartheta$ is the surface area of a spherical ring of height $\Delta h_i = r_0 \sin(\vartheta_i)\, \Delta\vartheta$ (Fig. 4), and $\varrho_0\, c$ is the specific resistance of air.

If $\Delta S_i = \Delta S =$ const, and this occurs when $\Delta h_i = \Delta h =$ const, expression (47) takes a form which is convenient for calculation

$$N_a = \frac{2\pi r_0 \Delta h}{\varrho_0 c} \sum_{i=1}^{m} p^2(\vartheta_i). \tag{48}$$

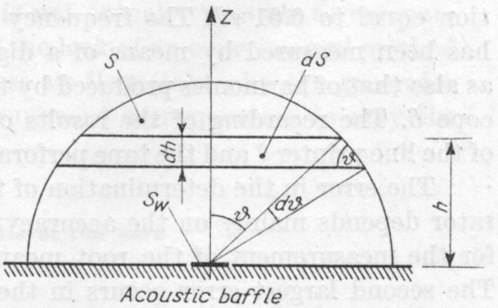

Fig. 4. Geometrical illustration of the determination method of the generator sound power

The angles ϑ_i at which the measurements of the acoustic pressure should be made are defined by the relation

$$\vartheta_i = \arccos(1 - i/m), \tag{49}$$

where $i = 0, 1, \ldots, m$.

Measurements of the sound power of the generator have been carried out in an anechoic chamber *10* (Fig. 5) using an apparatus composed of a 1/4″ — condenser microphone *1*, an analyser *2*, and a digital voltmeter *3*. The microphone was placed a distance of 0.9 m from the horn outlet of the generator and fixed to the arm. The latter permits rotation of the microphone, from the outside of the chamber, in a plane passing through the main axis of the generator through an angle of $\pi/2$ *rd*. The analog to digital convertor being coupled to the axis of rotation of the arm while cooperating with the reversion counter *4*, enables digital measurement of the angle of the microphone with a resolu-

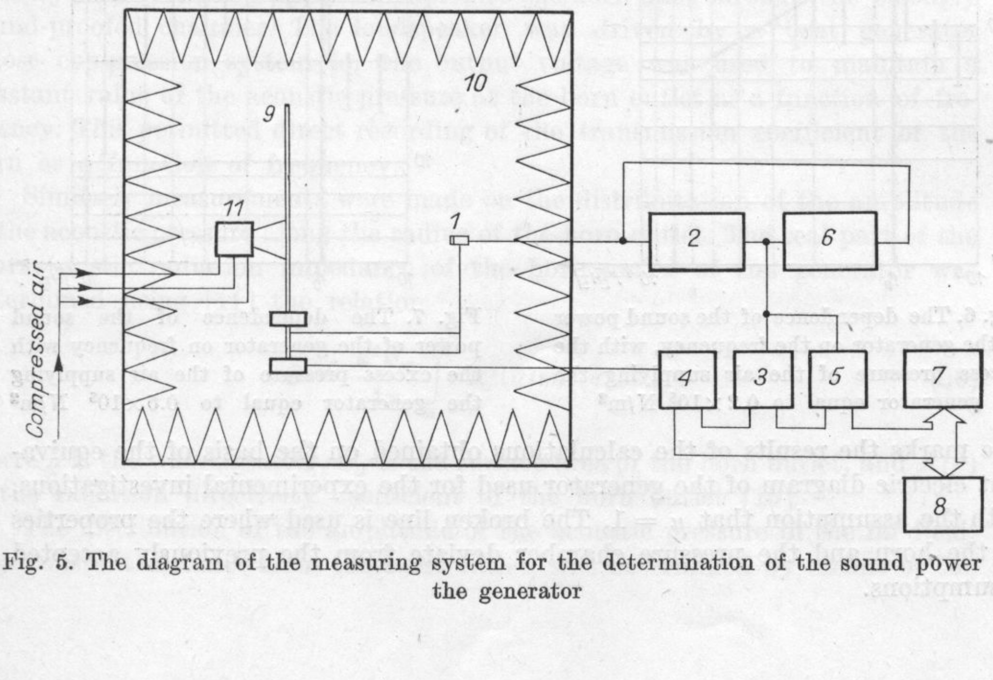

Fig. 5. The diagram of the measuring system for the determination of the sound power of the generator

tion equal to 0.01 *rd*. The frequency of the wave produced by the generator has been measured by means of a digital frequency meter *5*, while its shape as also that of harmonics produced by the generator was observed on the oscilloscope *6*. The recording of the results of the measurements was done by means of the line printer *7* and the tape perforator *8*.

The error in the determination of the value of the sound power of the generator depends mainly on the accuracy of the calibration of the apparatus used for the measurement of the root mean square value of the acoustic pressure. The second largest error occurs in the approximate numerical method for determining the value of the definite integral which occurs in the formula for the sound power of the generator (46). The magnitude of this error depends mainly on the length of the integration increment Δh. In the measurements carried out with a confidence level of 0.95, the relative error with which the value of the sound power of the generator could be determined did not exceed 19 %.

The results of the measurements of the sound power of the generator as a function of frequency for the excess pressures of the generator air supply of 0.2 and 0.5×10^5 N/m are shown in Figs. 6 and 7. In these figures a continuous line marks the results of the calculations obtained on the basis of the equivalent electric diagram of the generator used for the experimental investigations, with the assumption that $\mu = 1$. The broken line is used where the properties of the horn and the pressure chamber deviate from the previously accepted assumptions.

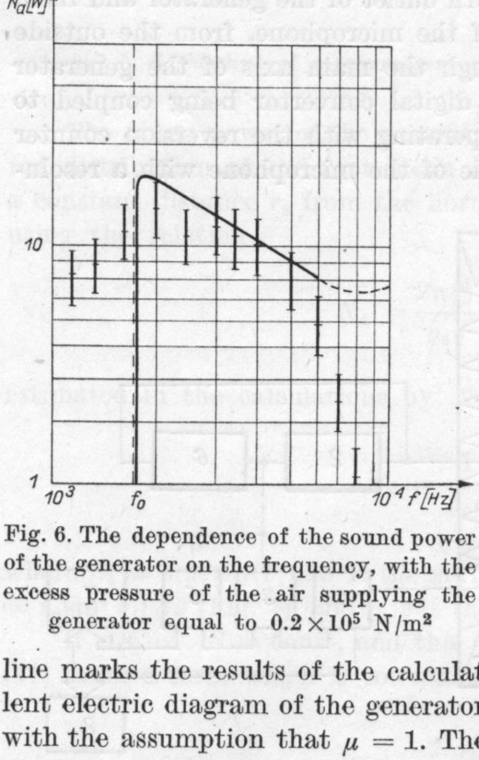

Fig. 6. The dependence of the sound power of the generator on the frequency, with the excess pressure of the air supplying the generator equal to 0.2×10^5 N/m^2

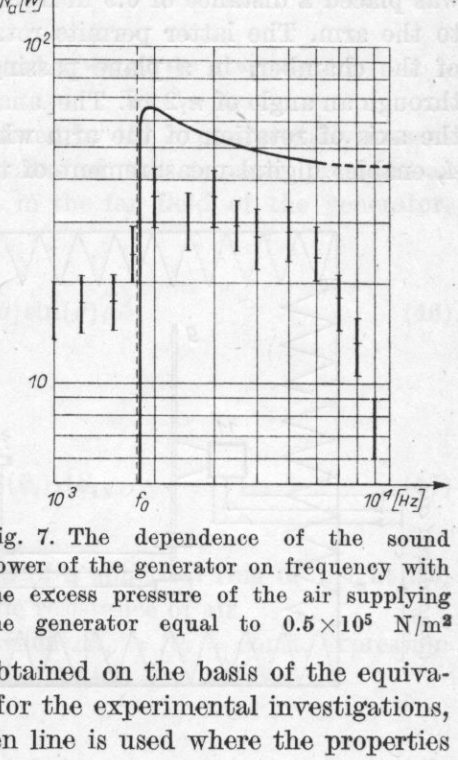

Fig. 7. The dependence of the sound power of the generator on frequency with the excess pressure of the air supplying the generator equal to 0.5×10^5 N/m^2

In conclusion, it can be stated that it is not actually possible to compare the supply power of the generator because of the lack of an experimental method permitting definition of the share in the mass air flow (taken by the generator from the compressor supplying it) of the component corresponding to only the first harmonic of the acoustic pressure [8].

6. Transmission properties of the horn

In view of the lack of definition of the range of application of relevant theoretical considerations, as has already been indicated in the theoretical part, experimental investigations have been carried out regarding the transmission properties of the horn of the generator. Their main aim was the determination of the range in which it is possible to propagate exclusively a tangential wave mode of the zero order in the horn of the generator. It has been assumed that the plane wave propagates in the horn over the frequency range in which the following criteria are simultaneously satisfied:

(i) the impedance of the radiation of the horn outlet as a function of frequency is that described by RAYLEIGH [15],

(ii) the distribution of the amplitude of the acoustic pressure on the surface of the horn outlet does not depend on position,

(iii) the modulus of the transmission coefficient of the horn (39) does not depend on the frequency

The investigations were carried out in an anechoic chamber, with the horn outlet placed in a plane acoustic baffle. A sound wave was radiated into the horn by means of a loudspeaker coupled to the horn inlet through the strongly sound-proofed chamber. The loudspeaker was driven by a beat generator whose compression system for the output voltage was used to maintain a constant value of the acoustic pressure at the horn outlet as a function of frequency. This permitted direct recording of the transmission coefficient of the horn as a function of frequency.

Similarly measurements were made on the distributation of the amplitude of the acoustic pressure along the radius of the horn outlet. The real part of the characteristic radiation impedance of the horn outlet of the generator was determined using [11] the relation

$$\Theta = \frac{k^2 S_w}{4\pi} \int_0^{\pi/2} R^2(\vartheta)\sin(\vartheta)\,d\vartheta, \tag{50}$$

where k is the wave number, S_w is the surface area of the horn outlet, and $R(\vartheta)$ is the radiation directivity coefficient of the horn outlet [15].

The distribution of the amplitude of the acoustic pressure in the far field, at a constant distance from the horn outlet, was determined by means of the apparatus used previously for the determination of the sound power of the generator. The value of the definite integral in expression (50) was calculated by SIMPSON's method on a digital computer. Each of the results of the calculations was based on 76 measurements of the acoustic pressure.

Figs. 8, 9 and 10 show in succession the results of the measurements of the real part of the characteristic radiation impedance of the horn outlet as a function of frequency, the amplitude distribution of the acoustic pressure along the

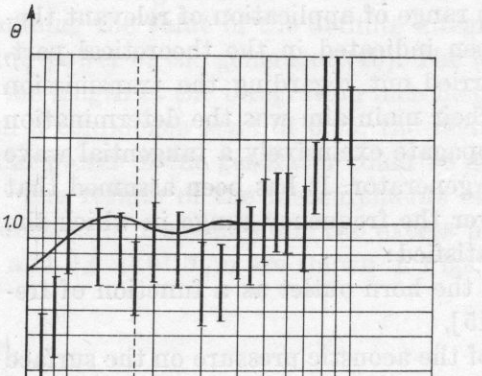

Fig. 8. The dependence of the real part of unitary relative impedance of the radiation of the horn outlet on the frequency

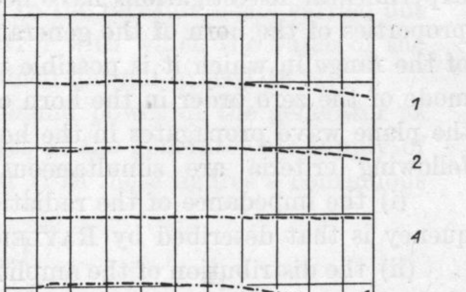

Fig. 9. The distribution of the amplitude of the acoustic pressure along the radius of the horn outlet

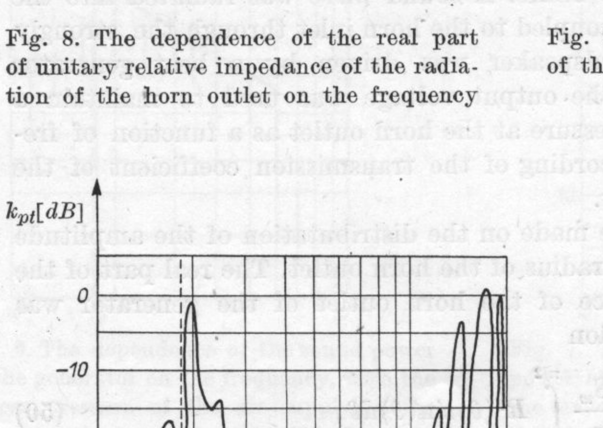

Fig. 10. The dependence of the transmission coefficient of a catenoidal horn with an annular cross-section on the frequency

radius of the horn outlet, and the the transmission coefficient of the horn as a function of frequency.

On the basis of the criteria accepted previously, and the results of the measurements it can be said that the propagation of a plane wave at frequencies up to 8 kHz is possible in the horn of the dynamic generator. Above this frequency wave modes of higher orders are produced in the horn.

7. Conclusions

On the basis of the measurement results it can be said that the model of the dynamic generator used for the theoretical considerations is correct for the limited range of conditions accepted at its formation, i.e. for small values of the air pressure in the pressure chamber (smaller than 0.2×10^5 N/m^2), and for the frequency range in which only plane wave propagation is possible in the acoustic system of the generator. The reason for the observed drop in sound power should be looked for in the resonance properties of the pressure chamber, and the stator passage, as well as in the formation of higher wave modes in the horn and pressure chamber of the generator.

The influence of the above-mentioned factors on the acoustic parameters can be reduced by the use of

(i) the largest number of passages in the stator,
(ii) stator passages as short as possible,
(iii) a strongly absorbing end to the pressure chamber,
(iv) slightly opened horns of.

The satisfaction of the above-mentioned criteria in the construction of a dynamic generator permits the optimal operation of the generator over a wide frequency range.

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Received on 11th May 1977

ARCHIVES OF ACOUSTICS
3, 1, 35-48 (1978)

VISCOELASTIC RELAXATION IN A SERIES OF FLUOROPROPYLMETHYLSILOXANE FLUIDS

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The paper presents the results of measurements of the shear impedance for samples of synthetic oil with different length of molecules for the shear frequencies 10, 30 and 450 MHz over a range of temperatures from −100° C do 50° C. It was found that the results of measurements of the shear impedance are well described by LAMB's liquid model with the high-frequency approximation for the DAVIDSON-COLE term

$$J^*_{j\omega} = J_\infty\left(1+\frac{1}{j\omega\tau_m}\right)+\frac{2KJ_\infty}{(j\omega\tau_m)^\beta}.$$

It has been shown that the coefficient $2K$ in this term is a function of the viscosity of the examined liquid. The results obtained have been interpreted as the superposition of two relaxation processes, one of high-frequency viscoelastic relaxation and one of low-frequency retardation related to the three-dimensional orientation of the molecules. The values of the individual relaxation times have been determined with the aid of ROUSE's theory.

1. Introduction

In recent years a number of lubricating liquids have been commonly used. These are mostly either oils with an addition of polymers which modifies their temperature viscosity characteristics, or completely synthetic oils. Amongst the latter are the most popular silicone liquids due to their small temperature viscosity coefficient and the comparatively low temperature of transition into a glassy state.

In order to know more closely the behaviour of oils as a function of the strain frequency the viscoelastic properties of a selected silicone oil (trifluoropropylmethylsiloxane) were investigated using ultrasonic shear strain. For these investigations oil samples with different lengths of macromolecular chain have been used to determine the influence of the chain length on the rheological properties of the oil.

Similar measurements of the viscoelastic properties have been made with polydimethylsiloxane oils [1]. However, because of the occurrence of crystallization during the cooling of the samples, neither the measurement of their limiting shear elasticity nor the investigation of the high-frequency part of the viscoelatic relaxation process was possible. Instead, the full range of the viscoelastic relaxation in poly-n-butylacrylates and poly-ethylacrylates has been examined. It was found in these liquids that at high frequencies the process of the viscoelastic relaxation can be described by means of a phenomenological formula for the compliance of the liquid to shear $J_{j\omega}$, in the form

$$J^*_{j\omega} = J_\infty\left(1+\frac{1}{j\omega\tau_m}\right)+\frac{2KJ_\infty}{(j\omega\tau_m)^\beta}, \tag{1}$$

where $J^*_{j\omega}$ is a complex compliance at an angular frequency $\omega = 2nf$, J_∞ ($=1/G_\infty$) is the limiting high frequency shear compliance, and τ_m is the Maxwell relaxation time, equal to ηJ_∞, with η being the static viscosity of the liquid. The coefficients β and K are numerical parameters.

Equation (1) was proposed by LAMB and others [3] for the purpose of describing the results of measurements of the shear compliance of plain liquids ($K = 1$ and $\beta = 0.5$) and liquid mixtures ($K \neq 1$ and $\beta = 0.5$). Subsequent measurements made on polymer liquids have shown that the parameter β is a function of the distribution of the liquid relaxation times and may vary from 0 to 1 [4, 6].

The last term of (1) is a modification of the empirical high frequency equation stated by DAVIDSON-COLE [5] who have made measurements of the dielectric permittivity of a liquid $\varepsilon^*_{j\omega}$ as a function of the frequency ω. They described the results of their measurements by an equation of the form

$$\varepsilon^*_{j\omega}-\varepsilon_0 = \frac{\varepsilon_0-\varepsilon_\infty}{(1+j\omega\tau)^\beta}, \tag{2}$$

where ε_0 is the value of the static dielectric constant of the liquid, ε_∞ is the limiting value at very low frequencies, τ is the dielectric relaxation time, β is the selected numerical parameter and ω is the angular frequency.

If the stress induced in a liquid does not come from an electric field as in the measurements by Davidson-Cole, but instead is caused by mechanical shear waves, the mechanical compliance of the liquid $J^*_{j\omega}$ can be described in a similar manner,

$$J^*_{j\omega} = J_\infty+\frac{J_r}{(1+j\omega\tau_r)^\beta}, \tag{3}$$

where τ_r is the time of retardation related to the reconstruction of the space orientation of the liquid molecules, and J_r is the retardation susceptibility.

The mechanical shear stress, in addition to the space reorientation of molecules also compels them to perform translational motion. If we describe this motion by the Newtonian susceptibility, Eq. (3) takes the form

$$J^*_{j\omega} = J_\infty + \frac{1}{j\omega\eta} + \frac{J_r}{(1+j\omega\tau_r)^\beta}. \tag{4}$$

For the majority of the examined polymer liquids, with medium and large viscosity coefficients, $\tau_r > \tau_m$. This permits the value of unity to be neglected in relation to the value $\omega\tau_r$. Equation (4) thus reduces to equation (1), with

$$J_r = 2KJ_\infty\left(\frac{\tau_r}{\tau_m}\right)^\beta. \tag{5}$$

2. The method of measurement

The method of measurement consist in defining the mechanical shear impedance of the liquid using transversel ultrasonic vibrations of frequency ω. The relation between the impedance $Z^*_{j\omega}$ and the complex modulus of elasticity of the liquid at this frequency $G^*_{j\omega}$ is of the form

$$Z^*_{j\omega} = \varrho G^*_{j\omega}, \tag{6}$$

where ϱ is the density of the liquid.

The mechanical shear impedance is preferably determined by the measurement of the amplitude refraction coefficient k and of the phase θ of the ultrasonic wave at the interface of two media, i.e. of a solid and a liquid. With a plane wave normally incident onto the interface, the mechanical shear impedance of a liquid is equal to

$$Z^*_{j\omega} = Z_Q\frac{1-k^2+j2k\sin\theta}{1+k^2+2k\cos\theta}, \tag{7}$$

where Z_Q is the impedance of the solid.

For most of the liquids the phase shift of a wave related to the reflection is small since the impedance of a liquid $Z < 0.1\,Z_Q$. Thus it can be assumed that $\cos\theta = 1$. Equation (7) then takes the form

$$Z^*_{j\omega} = R + jx = Z_Q\left(\frac{1-k^2}{(1+k)^2} + j\frac{2k\sin\theta}{(1+k)^2}\right). \tag{8}$$

The error caused by assuming $\cos\theta = 1$ is smaller than 1%. Equation (8) permits the evaluation of the real part of the impedance knowing only the amplitude reflection coefficient:

$$R = Z_Q\left(\frac{1-k}{1+k}\right). \tag{9}$$

Knowing the values R and X of the components of the shear modulus of elasticity of the liquid $G^*_{j\omega}$ can be evaluated from (6):

$$G'_\omega = \frac{R^2-X^2}{\varrho}, \tag{10}$$

$$G''_\omega = \frac{2RX}{\varrho}. \tag{11}$$

In this paper measurements were made at frequencies of 10, 30 and 450 MHz. The measuring system and more particulars related to the measurements at the frequencies 10 and 30 MHz can be found in a previous paper [7], while those for the frequency 450 MHz elsewhere [8].

3. Specification of the samples investigated

The oil to be tested was trifluorpropylmethylsiloxane (FS 1265), a product of Midland Silicone Limited (U. K.) with a structural formula $(CH_3)_3SiO(CH_3SiO(H)_2CF_2)_nSi(CH_3)_3$. This liquid is a linear polymer, free of main chain branches. The measurement involved four samples of this oil which differed only in their chain lengths (i.e. the value of n in the structural formula).

The static viscosity at room temperature (20°C), then mean numerical molecular mass $\bar{M}_n$ and the ratio $\bar{M}_w/\bar{M}_n$, of the individual oil samples were

sample	η [P]	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
A	1.72	1720	1.12
B	30.0	9050	1.19
C	179.0	20000	1.41
D	8120.0	72600	1.84

A mixture comprising samples B and C in the ratio 0.3 B +0.7 C was also tested. The viscosity of this sample at room temperature was BC 113.0 poises.

The measurement of the molecular mass and its distribution in the four main liquid samples was performed by the Rubber and Plastics Research Association (RAPRA) at Screwbury in Great Britain. The spectra of the distribution of the molecular mass of the individual samples as obtained by RAPRA are shown in Fig. 1.

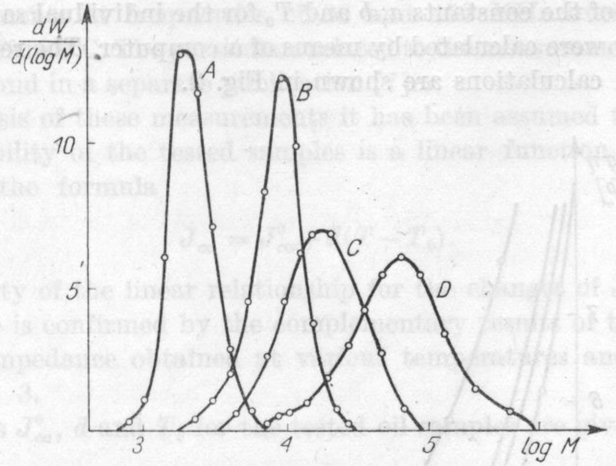

Fig. 1. The spectrum of the distribution of the molecular mass $\bar{M}$ of the samples A, B, BC, C and D of the tested oil

4. Experimental results

4.1. *Measurements of the density as a function of temperature.* These were made using a picnometer. It was found that there was a linear relationship of the density changes of the tested samples over a temperature range from −70°C to 50°C in agreement with the equation

$$\varrho_{(T)} = \varrho_0[1-\alpha_0(T-T_0)]. \tag{12}$$

The values of ϱ_0 α_0 and T_0 for particular oil samples are given in Table 1.

Table 1

Sample	$\alpha_0(\times 10^4)$	a	b	$J^0_\infty \times$ [10^9m^2/N]	d	T_0[K]
A	1.3515 7.4	−6.03	932.1	0.2	0.112	151.6
B	1.3707 5.83	−4.58	1100.4	0.154	0.125	156.0
C	1.3945 6.02	−2.62	1016.1	0.297	0.0627	163.0
BC	1.391 6.04	−3.45	1116.7	0.118	0.1523	156.6
D	1.4315 6.99	−1.12	997.6	0.331	0.057	166.6

4.2. *Measurements of the viscosity as a function of temperature.* The measurements were made with the aid of a capillary viscosimeter over a temperature range from −50°C to 50°C. It was found that that changes in the viscosity of the tested samples as a function of temperature can be described using the equation

$$\ln\eta = a+\frac{b}{T-T_0}. \tag{13}$$

The values of the constants a, b and T_0 for the individual samples are given in Table 1. They were calculated by means of a computer. The results of the measurements and calculations are shown in Fig. 2.

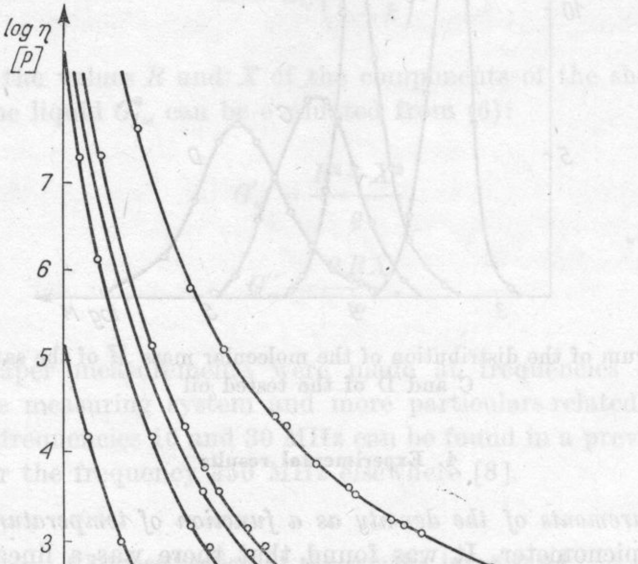

Fig. 2. The results of measurements and calculations (continuous line) of the viscosity η of the tested oil samples as a function of temperature

4.3. *Measurement of the limiting shear compliance as a function of temperature.* With satisfactorily high frequencies the reaction of a liquid to shear strain is purely elastic, whereas the shear modulus of elasticity (known as the limiting modulus) is comparable with the modulus of elasticity of a solid. This area is accessible for measurement over a temperature range in which the liquid is super cooled state i.e. between the temperature of the transition into a glassy state and the temperature at which the viscoelastic relaxation becomes predominant.

The limiting value of shear elasticity G_∞, and strictly speaking the inverse of this magnitude, the limiting shear compliance J_∞ was defined from ultrasonic measurements at frequencies of 30 and 450 MHz over a temperature range from −100 to 0°C. The particulars related to the measurement of this magnitude can be found in a separate publication [7].

On the basis of these measurements it has been assumed that the limiting shear susceptibility of the tested samples is a linear function of temperature, according to the formula

$$J_\infty = J_\infty^0 + d(T - T_0). \tag{14}$$

The validity of the linear relationship for the changes of J_∞ as a function of temperature is confirmed by the complementary results of the measurement of the shear impedance obtained at various temperatures and frequencies as shown in Fig. 3.

The values J_∞^0, d and T_0 for the tested oil samples are given in Table 1.

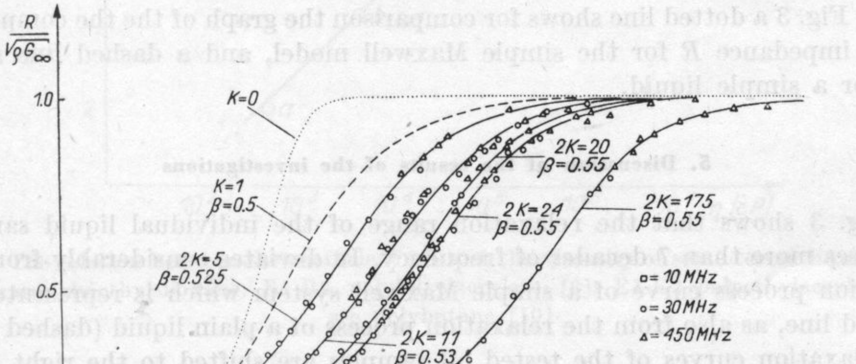

Fig. 3. Comparison of the results of the real impedance R_L in a normalized scale. Continuous and broken lines are plotted from equation (1). Notation can be found in the text

4.4. *Measurement of the real component of the impedance.* The measurement of the real component of the acoustic shear impedance was made at frequencies of 10, 30 and 450 MHz over a temperature range from −50°C to 50°C. For each temperature two measurements of the refraction coefficient k were made, the first for a quartz bar with a free end and the second with the end of the bar immersed in a liquid sample. The difference in attenuation of the first ten pulses that are echoes of repeated reflections in the bar are defined by comparison with a standard pulse of controlled amplitude. The values of the resistance were then defined from formula (9). The accuracy of measurement of R was ± 400 [g/s cm²] for a frequency of 450 MHz and ±2400 [g/s cm²] for the frequencies 10 and 30 MHz.

The results of these measurements are shown in Fig. 3. For the purpose of an orderly presentation of the results use has been made of the method of the replacement of variables [9]. This makes it possible to present the results of measurements made at various frequencies and temperatures in the form of one curve as a function of frequency normalized to the relaxation frequency of the Maxwell model ($1/\omega_0 = \eta J_\infty$). Thus changes in the impedance of a liquid over a wide frequency range and easy comparison of the results obtained for various liquids can be presented.

Also for this reason the values of the component of the impedance R on the vertical axis have been referred to the acoustic impedance in the limit of infinitely large frequencies (i.e. equal to $\sqrt{\varrho G_\infty}$). The continuous lines that approximate the results of measurements have been calculated from formula (1) by selecting on the computer the corresponding values of k and β for the individual oil samples. These values are given in Table 2.

In Fig. 3 a dotted line shows for comparison the graph of the the component of the impedance R for the simple Maxwell model, and a dashed line shows that for a simple liquid.

5. Discussion of the results of the investigations

Fig. 3 shows that the relaxation range of the individual liquid samples comprises more than 7 decades of frequency. In deviates considerably from the relaxation process curve of a simple Maxwell system which is represented by a dotted line, as also from the relaxation process of a plain liquid (dashed line). The relaxation curves of the tested oil samples are shifted to the right along the frequency axis. Parallel displacements of the curve are the greater with higher values of the static viscosity of the tested sample. The shape of the relaxation curve, being similar to that of a plain liquid, and its displacement, show that in addition to the relaxation process characteristic of a simple liquid there also occurs and additional factor which causes the displacement of the measuring points to the right on the frequency scale. The amount of this displacement is defined by the coeficient $2K$ in formula (1). A good approximation to the value of this coefficient, when β is near to 0.5, is given by equation (15) [13]

$$\log 2K = k\eta^{0.146}, \tag{15}$$

where η is the static viscosity in centipoise, k is a constant coefficient equal to one third for the oil samples tested. It was found that the relationship (15) is also valid for polybutane polymers [10] when $k = 1/8$, and for polyacrylate polymers [2] when k is near to 1/6. This is shown in Fig. 4. The point $E2$ for a sample of polyacrylate polymer is beyond the straight line, probably because of its large molecular mass ($M_n = 22\,000$) and because of some entanglement resulting from this. This consideration also applies to sample D of the tested oils ($M_n = 72\,600$).

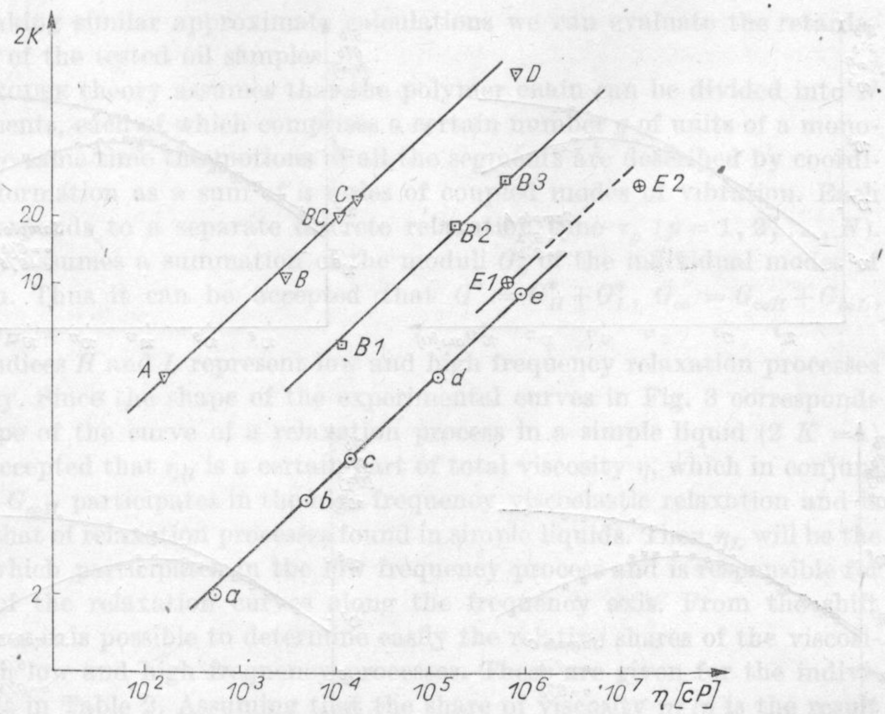

Fig. 4. The relation between the coefficient $2K$ and the viscosity of some tested liquids. A-D trifluorpropylmethylsiloxane, B1-B3 polybutylacrylate [2], E1-E2 polyethylacrylate [2], a-e polybutane [10]

Since the value $2K$ is related to the viscosity by equation (15), expression (5) for the retardation susceptibility, in its dependence on the viscosity of the tested oil, can be written in the form

$$\log J_r = \log J_\infty + \frac{1}{3}\eta^{0.146} + \beta \log \frac{\tau_r}{\tau_m}, \tag{16}$$

φ_r can be defined on the basis of ROUSE's theory.

With the measured values of the real component of the impedance as a function of temperature and frequency, and with the value of imaginary component of the impedance it is possible to calculate the dependence of the components of the modulus of elasticity G' and G'' as functions of frequency. The results for the particular samples are shown in succession in Figs. 5-8. On the vertical axis are values of the moduli normalized by means of the coefficient b, while on the horizontal axis are values of frequency which have been normalized by means of the coefficient a. Practical reasons support the use of such normalization which was introduced by FERRY [9]. The normalization coefficients are

$$b = \frac{\varrho T}{\varrho_* T_*}, \quad ab = \frac{\eta}{\eta_*}, \tag{17}$$

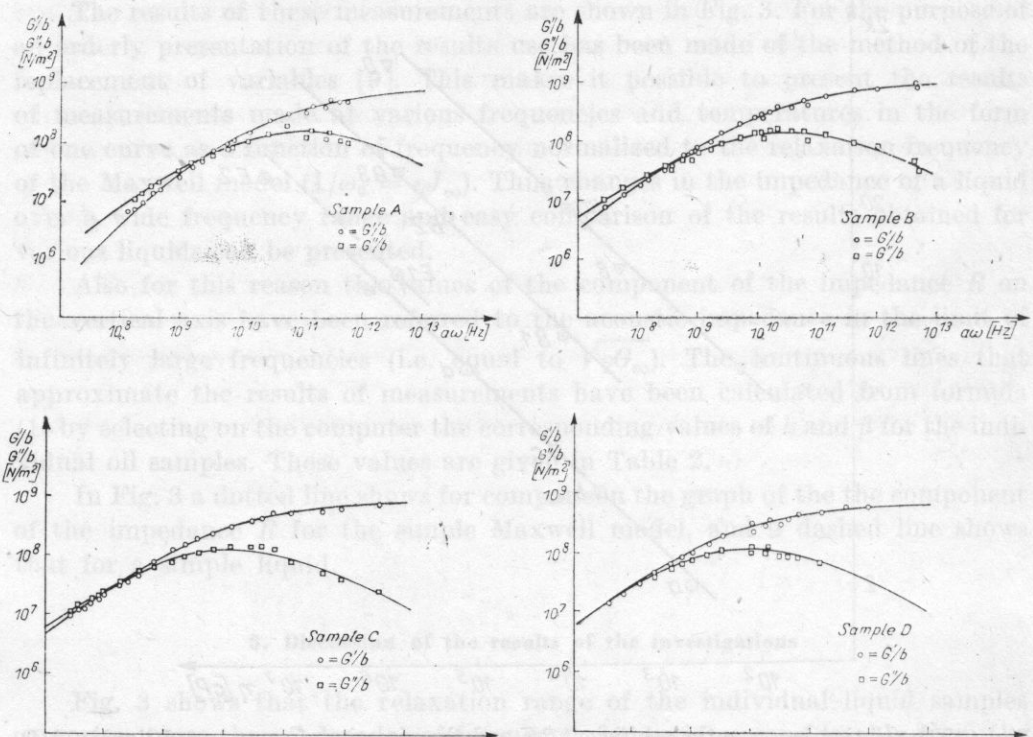

Fig. 5-8. The dynamic modulus G' and the loss modulus G'' of the individual oil samples as functions of frequency. The continuous line is the curve of equations (1) and (6), a and b are normalization coefficients

where ϱ, T and η are the density, the temperature (in deg. Kelvin) and the viscosity respectively, while the magnitudes with an asterisk are the values at the reference temperature. It has been assumed that this is a temperature of 20°C (293.1 K). For this temperature the coefficients a and b are equal to unity.

Figs. 5-8 show that the values of the conservative modulus G' increase asymptotically with increasing frequency up to $10^9\ \mathrm{N/cm^2}$, whereas the loss modulus G'' attains a maximum. The highest value of the loss modulus is one order of magnitude smaller than the limiting of the conservative modulus. The intersection of the curves, at which the values of both moduli become equal ($\tan\ \delta = 1$) shifts towards lower frequencies with increasing viscosity of the tested sample. This is probably attributable to the increase in retardation when the length of a molecule increases.

The behaviour of a molecule in the range of retardation relaxation can be represented in a similar way to that accepted for the previously tested polydimethylsiloxane oil [1]. To describe the results use was made there of ROUSE's theory. Making similar approximate calculations we can evaluate the retardation times of the tested oil samples.

The ROUSE theory assumes that the polymer chain can be divided into N equal segments, each of which comprises a certain number q of units of a monomer. At the same time the motions of all the segments are described by coordinate transformation as a sum of a series of coupled modes of vibration. Each mode corresponds to a separate discrete relaxation time τ_p ($p = 1, 2, \ldots, N$). This theory assumes a summation of the moduli G_p of the individual modes of the motion. Thus it can be accepted that $G^* = G_H^* + G_L^*$, $G_\infty = G_{\infty H} + G_{\infty L}$, $\eta = \eta_H + \eta_L$.

The indices H and L represent low and high frequency relaxation processes respectively. Since the shape of the experimental curves in Fig. 3 corresponds to the shape of the curve of a relaxation process in a simple liquid ($2\ K = 1$) it can be accepted that η_H is a certain part of total viscosity η, which in conjunction with $G_{\infty H}$ participates in the high frequency viscoelastic relaxation and is similar to that of relaxation processes found in simple liquids. Then η_L will be the viscosity which participates in the low frequency process and is responsible for the shift of the relaxation curves along the frequency axis. From the shift of the curves it is possible to determine easily the relative shares of the viscosities in both low and high frequency processes. These are given for the individual liquids in Table 2. Assuming that the share of viscosity η_L/η is the result of the existence of p ROUSE modes, it is possible to determine the value of p for the individual oil samples. The values of p have been calculated on a computer and are also given in Table 2.

Table 2

Sample	$2\ K$	β	p	η_L	η_L/η	η_H
A	5	0.525	2	1.23	0.715	0.49
B	10.5	0.53	7	27.6	0.92	2.4
C	24	0.55	30	175.4	0.98	3.58
BC	20	0.55	20	109.8	0.9717	3.14
D	175	0.55	500	8115.5	0.99944	4.5

The values stated in Table 2 permit to evaluation of the high frequency relaxation times τ_H, and the low frequency relaxation times τ_L for the individual liquid samples, as well as the value of the retardation compliance J_r. The values of τ_L have been calculated from formula (11),

$$\tau_L = \tau_{p_i \ldots N} = \frac{\pi^2}{4N^2} \frac{\eta \bar{M}_n}{\varrho RT \sum\limits_p \frac{1}{p^2} \sin^2 \frac{p\pi}{2N+1} \left(\frac{\bar{M}_w}{\bar{M}_n} \right)} \tag{19}$$

for liquid samples A and B, while for the other samples in view of the satisfactorily large number, N, of the Rouse modes, use has been made of the simplified formula

$$\tau_{p_i} = \frac{6\eta M_i}{\pi^2 p^2 \varrho RT(M_w/M_i)}. \tag{20}$$

In both cases $M_w = \Sigma M_i W_i$ is the mean (by weight) molecular mass of the polymer, ϱ is the density of liquid, R is the gas constant, T is the temperature in degrees of Kelvin, and $N = pq$.

In the computations it has been assumed that the number of monomer units $q = 5$ corresponding to 7 atoms of silicon in a segment. This value is assumed for the bonds Si-O which exhibit an exceptionally high susceptibility to bending [12]. However, it can be proved that the value of q is not critical in the computations.

The values of the relaxation times and of the compliance calculated from formulae (19) and (20) are given in Table 3. Since the spectrum of the Rouse modes is a discrete spectrum, and the spectrum of Lamb liquid model is a continuous spectrum [10], it is difficult to illustrate the superposition of both spectra. However, it can be noticed that in each case the relaxation times of the Rouse modes are considerably lower than the high frequency relaxation times.

Table 3

Sample	$\varphi_H(\times 109)$	φ_{r_1}	$\varphi_{r_N}(\times 109)$	J_r/J_∞	J_r	φ_r/φ_m
A	0.165	1.1×10^{-7}	140	110	3.7×10^{-8}	196
B	0.677	7.8×10^{-6}	240	410	1.2×10^{-7}	925
C	0.977	5.1×10^{-5}	57	900	2.5×10^{-7}	1000
BC	0.88	2.0×10^{-5}	49	852	2.3×10^{-7}	667
D	1.22	1.4×10^{-3}	8	5900	2.8×10^{-6}	640

The identical shape of the curve in the range of viscoelastic relaxation in simple liquids (i.e. with comparatively short molecules) can be explained by the fact that at high frequencies the only motions likely to occur in the long molecule are vibrations of the side groups of a polymer chain.

Thus it seems to be justified to accept that the retardation time τ_r corresponds to the longest time of relaxation (τ_{L_i}) in the Rouse modes of vibration since in this case all of the molecule participates in the process of reorientation.

It should also be noticed that as the length of the polymer chain increases there is also an increase in the polymer susceptibility to bending and the ratio J_r/J_∞ (Fig. 9). This is physically substantiated. The limiting compliance J_∞ is determined by the high frequency properties of liquid and is a characteristic magnitude for a given liquid, whereas the retardation compliance J_r is defined by the depth of the potential barier between polymer molecules. This potential barrier depends on the length of the polymer chain and reduces

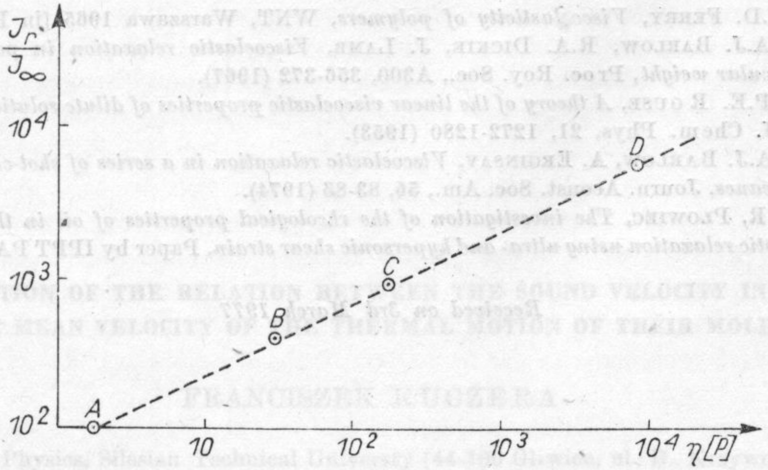

Fig. 9. The relation between the ratio J_r/J_∞ and the viscosity of the tested oil samples

with the increasing chain length. Consequently, J_r is higher for longer polymer chains. The character of the changes in J_r with increasing viscosity is defined directly by the coefficient $2K$ which is related to the viscosity of the tested samples by equation (15) since both the limiting compliance J_∞ and the ratio of the time of retardation to the time of relaxation differ only a little for the individual oil samples.

The execution of the above-decsribed measurements in the ultrasonic laboratory of the University of Glasgow (G. Britain) was made possible with the assistance of prof. J. Lamb for which one of the authors (R. P.) would like to express his sincere gratitude.

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Received on 3rd March 1977

ARCHIVES OF ACOUSTICS
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INVESTIGATION OF THE RELATION BETWEEN THE SOUND VELOCITY IN LIQUIDS AND THE MEAN VELOCITY OF THE THERMAL MOTION OF THEIR MOLECULES

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It is shown in this paper that in assuming a rectangular potential well we also assume that the intermolecular compressibility of a liquid consists of a kinetic and a potential part. It was accepted that the kinetic part – as for a perfect gas – is independent of temperature at constant pressure. Hence, it can be concluded that the temperature coefficients of both the compressibility and the sound velocity depend almost exclusively on the space filling.

In considering the propagation of acoustic waves in gases attention has long been drawn to the close similarity of the expressions for the acoustic velocity and the mean velocity of the thermal translatory motion of the molecules

$$w = \sqrt{\gamma \frac{RT}{M}} \tag{1}$$

and

$$c = r\sqrt{\frac{RT}{M}}, \tag{1a}$$

where w denotes the propagation velocity of acoustic waves in a gas, c is the mean velocity of thermal motions, and r is a constant coefficient whose value depends on the method of averaging used. Thus there is a close relationship between the propagation velocity of the acoustic waves and the velocity of the thermal motion although the relationship between r and γ in formulae (1) and (1a) has not yet been reported. (The solution to this problem will be presented in section 1). In this situation there arises an obvious an interesting question as to whether and in what manner the velocities of the thermal motion of molecules in liquids are related to the velocity of propagation of acoustic waves in liquids (¹). This paper contains remarks and observations concerning this problem. In the first place attention will be drawn to the relation between the propagation velocity of acoustic waves in perfect gases and the thermal velocity (s. 1). Then after a brief recapitulation of some essential problems concerning the propagation of acoustic waves in solids (s. 2) attention is turned to the propagation of acoustic waves in liquids (s. 3).

1. In first considering the propagation of an acoustic wave in a perfect gas from a microscopic point of view it can be seen that within a system of hard, non-interacting molecules a continuous wave cannot propagate. An acoustic wave propagates in gas as a result of the volume elasticity which in this case is of a purely kinetic and static nature.

Consideration must thus be given to the volumes of such size that statistical quantities become meaningful. (This is in contrast to the analogous problem in solids where it is possible to start with a model confined to one molecule and its nearest environment). We thus have

$$w^2 = \left(\frac{\partial p}{\partial \varrho}\right)_s = \gamma \left(\frac{\partial p}{\partial \varrho}\right)_T, \tag{2}$$

where $\gamma = c_p/c_v$, and w is the velocity of acoustic waves in the gas. The other letters have their commonly accepted meanings. The gas pressure p can be expressed by the formula

$$p = \frac{1}{3} n \, m\overline{c^2} = \frac{1}{3} \varrho \overline{c^2}, \tag{3}$$

where n denotes the number of molecules per cubic centimetre, m is the mass of one molecule, and $\overline{c^2}$ is the mean square velocity of the thermal motion of the molecules. From (2) and (3) it can be seen that

$$w^2 = \gamma \frac{1}{3} \overline{c^2} = \frac{1}{3} [\overline{c^2} + (\gamma - 1)\overline{c^2}]. \tag{4}$$

If the acoustic disturbance is an isothermal process then the velocity of propagation w_T of such a disturbance will be given by

$$w_T^2 = \frac{1}{3} \overline{c^2} = \frac{1}{3} \overline{(c_x^2 + c_y^2 + c_z^2)} = \overline{c_x^2} \pm \overline{c_y^2} \pm \overline{c_z^2}. \tag{5}$$

(¹) In using the term "liquid" we shall always mean simple liquids as we hold that the properties essential for the liquid state occur in a simple liquid in an undisturbed form. By taking into consideration various side-effects such as association, solvation, hydrogen binding etc., we unnecessarily complicate the problem if we are only interested in the essence of the liquid state.

The isothermal disturbance thus propagates at a speed whose square is equal to the mean square of the component of the velocity of the thermal motion in the direction of propagation of the acoustic waves.

In the case of an adiabatic disturbance the mean square velocity increases. We then have

$$w^2=\left(\frac{\partial p}{\partial \varrho}\right)_s=\frac{\partial}{\partial \varrho}\left(\frac{1}{3}\,\varrho\overline{c^2}\right)_s=\frac{1}{3}\left[\varrho\left(\frac{\partial \overline{c^2}}{\partial \varrho}\right)_s+\overline{c^2}\right]=\frac{1}{3}\left[\varrho\left(\frac{\partial \overline{c^2}}{\partial v}\right)_s\frac{\partial v}{\partial \varrho}+\overline{c^2}\right]. \qquad (6)$$

In this expression we do not know the change in the mean square of the velocity during the adiabatic deformations $(\partial c^2/\partial v)_s$. It can however be determined by the following considerations.

It is known that the internal energy of one mole of a perfect gas is given by the expression

$$U=Nf\,\frac{1}{2}\,kT=Nf\,\frac{m\overline{c^2}}{6}\,, \qquad (7)$$

where f denotes the number of degrees of freedom. We thus have

$$\left(\frac{\partial U}{\partial V}\right)_s=p\,. \qquad (8)$$

From (7) and (8) we obtain

$$Nf\,\frac{m}{6}\,\frac{\partial}{\partial V}\,(\overline{c^2})_s=\frac{1}{3}\,n\,m\overline{c^2}\,,$$

and thus

$$\frac{\partial}{\partial V}\,(\overline{c^2})_s=\frac{2\overline{c^2}}{fV}\,. \qquad (9)$$

Substituting (9) into (6) we obtain

$$w^2=\frac{1}{3}\left[\frac{2}{f}\,\overline{c^2}+\overline{c^2}\right]=\frac{1}{3}\,\overline{c^2}\left[\frac{2}{f}+1\right]=\ldots=\frac{1}{3}\,\overline{c^2}\gamma\,. \qquad (10)$$

2. There is a widely held view that the liquid state is more similar to the solid state than to the gaseous state. At the same time it is stressed that liquids and solids have very similar densities. Furthermore, it is considered that:

(a) the short-range order in liquids is a remnant of the long-range order in crystals,

(b) the thermal motion of the molecules in liquids is similar to the thermal motion of the molecules in solids.

As we shall subsequently discuss these assumptions, and particularly their acoustic aspects, in section 3, some short remarks on the problem of the thermal motion of molecules (a one element solid) and the propagation of acoustic waves are needed.

It is generally considered that this problem is covered by the theory of the specific heats of a one element solid. It is assumed in this theory that a model of a lattice of coupled harmonic oscillators (one per atom) correctly describes the thermal motion. The internal energy is obtained accordingly by summing the quantized energies at all frequencies. An actual solution of the problem is obtained by the use of either Debye's method or the Bern-Kármán method.

Having reviewed briefly these well-known facts it should be stressed that — independent of the fundamental importance of both the acoustic theories of the specific heat — their significance for the problem of the velocity of acoustic waves and thermal motion should not be overestimated. The limitation arise for, among others, the following reasons:

(a) Using Debye's method we proceed from the assumption of an elastic continuum. In such a manner we thus immediately preclude the possibility of considering the elementary (molecular) mechanism of the transmission of an acoustic pulse.

(b) Using the Born-Kármán method we neglect the finite volume of the atoms. This leads consistently to an erroneous representation of the intermolecular forces, as may be seen from the following argument.

Let the volume of a solid be V, of this V_M accounts for the proper volume of the molecules themselves. Let us call $V_s = V - V_M$, the free volume. We then have

$$\frac{\partial V}{\partial p} = \frac{\partial V_s}{\partial p} + \frac{\partial V_M}{\partial p}, \quad \frac{1}{V}\frac{\partial V}{\partial p} = \frac{V_s}{V}\frac{1}{V_s}\frac{\partial V_s}{\partial p} + \frac{V_M}{V}\frac{1}{V_M}\frac{\partial V_M}{\partial p},$$

that is

$$\beta = \frac{V_s}{V}\beta_s + \frac{V_M}{V}\beta_M. \tag{11}$$

From formula (11) it is evident that the measured (effective) compressibility β_M differs considerably from the "real" intermolecular compressibility β_s. The second term on the right-hand side of the equation can usually be neglected.

3. A relation between the velocity of propagation of acoustic waves in liquids and the thermal motion of the molecules should be based on the information already available on the thermal motion of molecules in liquids. Unfortunately, such information is very scarce and thus no theory of the specific heat of a one element liquid has so far been elaborated.

Following Frenkel [3] it has been suggested that the similar values of the specific heat c_v, of liquids and relevant solids in the neighbourhood of the solidification temperature, give evidence for the similarity of the thermal motion in both states. This information is too general for the present purpose since it conveys no clear idea as to whether the molecules are moving at a uniform speed while reflected from the walls of the cells formed by the closest molecules, or are vibrating sensu stricto, and are thus under the action of, for example harmonic, forces. However, the molecular mechanism of the propagation of acoustic waves in liquids depends on the nature of these motions. In the former case the propagation of an acoustic wave can to some extent be explained by reference to the "gas model", i.e. to the state presented in section 1. However, in the latter case use shoulds be made of the quasi-crystalline model.

Thus it can be clearly seen that even qualitative considerations concerning the elementary mechanism of the propagation of acoustic waves in liquids must be based on reliable information on the nature of the thermal motion of the molecules. It has been suggested that the existence of short range order in liquids points explicitly to the fact that an explanation of the manner in which acoustic waves propagate in liquids should be based on the quasi-crystalline model, the short range order being interpreted as an expression of the tendency of the intermolecular forces to develop crystalline structures. However, as long ago as 1922 Gans [4] showed that in systems of non-interacting rigid balls there is a distinct probability of finding the molecules at a definite distance from each other. This probability depends on amongst other factors the ratio V_s/V. From expression (11) it can be seen that the intermolecular "real" compressibility is considerably higher than the effective (measured) compressibility, than the assumption of a flat bottomed potential for the interacting forces of the molecules cannot be regarded as a course approximation. In assuming a flat potential bottom, i.e. assuming that the liquid molecules are moving freely from collision to collision, it can be supposed that the relationship between the wave propagation velocity and the mean velocity of thermal motion, substantiated in section 1, can also be used for a liquid [5].

However, this description is not satisfactory. If the liquid compressibility is considered to be exclusively of a kinetic nature, derived from the energy in a manner similar to that of the gas molecules, then by considerations of space filling, the relation

$$\beta = \frac{V_s}{V} \beta_s$$

should be satisfied, as can be seen from formula (11). Now the ratio V_s/V varies from approximately 1/5 to 1/10, and the liquid compressibility should thus be from 1/5 to 1/10 that of the gas compressibility. This obviously does not occur and it is therefore evident that even under the assumption of a flat potential well, the relationships derived in section 1 cannot be used for liquids. The main reason for this can be seen in the fact that the flat potential bottom lies below the axis of the abcissae, while the depth of the well depends also (under the condition of constant pressure that we are considering), on the temperature.

The physical conditions, represented by means of a geometrically simple potential are very complicated. It must be taken into consideration that it is not possible, in this case, to use the equipartition principle. The application of this principle requires that the energy of a molecule should be a linear homogeneous function of the squares of the position coordinates and of the momenta. It can be seen from the model that the liquid compressibility is both kinetic and potential. However, we do not know the way in which these two components combine to form the resultant compressibility. We can only make an estimate for subsequent use. We are of the opinion that the kinetic component of the intermolecular compressibility is considerably higher than the potential component, although the temperature dependence of the intermolecular compressibility is defined by the temperature dependence of the potential component. We thus can write

$$K_s = K_{sk} + K_{sp}, \tag{12}$$

where K_{sk} and K_{sp} denote the moduli of the kinetic and potential intermolecular compressibility, respectively.

Neglecting the compressibility of the molecules themselves, the measured compressibility β can, using formula (11), take the form

$$\beta = \frac{V_s \beta_s}{V}. \tag{13}$$

The question arises as to the relation of the change of the ratio V_s/V to the change in the compressibility β, and the dependence of this effect on temperature at constant pressure. It can be seen that

$$\frac{1}{\beta}\frac{\partial\beta}{\partial T} = \frac{1}{V_s}\frac{\partial V}{\partial T} - \frac{1}{V}\frac{\partial V}{\partial T} + \frac{1}{\beta_s}\frac{\partial\beta_s}{\partial T}$$

or, by neglecting the third term on the right-hand side of the above equation,

$$\frac{1}{\beta}\frac{\partial\beta}{\partial T} = \left(\frac{V}{V_s} - 1\right)\alpha, \tag{14}$$

where α denotes the volume expansion coefficient.

From formula (14) it is evident that the temperature dependence of the change in the measured compressibility β is defined almost exclusively by a change in the space filling. Table 1 contains numerical data of the relevant coefficients. From the table it can be seen, that for benzene, for example, $\beta^{-1}(\partial\beta/\partial T_p \times \alpha^{-1} \simeq 6$, in agreement with the values obtained by other methods (²).

(²) The values of the volumes of the actual molecules determined by various methods differ slightly from one to another because it is evident that the quantity to be measured is defined by the method of measurement. In this interpretation we consider that, for example, two values of the ratio V_S/V equal to 1/6 and 1/7, respectively, are in agreement.

Table 1. Thermal coefficients of some normal liquids

Name of liquid	$\frac{1}{\beta}\left(\frac{\partial\beta_T}{\partial T}\right)_p \times 10^4$ [deg^{-1}]	$\frac{1}{w}\left(\frac{\partial W}{\partial T}\right)_p \times 10^4$ [deg^{-1}]	$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \times 10^4$ [deg^{-1}]	$\frac{1}{\gamma}\left(\frac{\partial \gamma}{\partial T}\right)_p \times 10^4$ [deg^{-1}]
Benzene	+74.6 [6]	−35.5 [7]	12.2 [8,9]	−7.4 [10] −6.6*
Carbon tetrachloride	+73.0 [6]	−33.7 [7]	12.2 [8,9]	−6.1 [10] +2.5*
Ethyl ether	+99.2 [6]	−46.3 [7]	16.4 [8,9]	−0.5 [10]
Carbon disulphide	+77.4 [6]	−27.9 [7]	12.0 [8,9]	+10.8 [10] +9.2*
Ethylo-benzene	+57.8 [11]	−28.4 [7]	10.1 [8,9]	−3.3*
Chloro-benzene	+57.3 [6]	−28.8 [7]	9.8 [8,9]	−8.6 [10] −3.8*
Cyclohexane	+78.1 [9]	−36.0 [7]	12.0 [8,9]	−9.8 [12]
Aminobenzene	+50.0 [6]	−24.4 [7]	8.5 [8,9]	−2.3 [8,9] −1.5*
Ethyl acetate	+88.5 [9]	−38.3 [7]	13.6 [8,9]	−2.4 [8,9]
n-pentane	+99.2 [9], [13]	−44.5 [7]	16.2 [13]	−5.4*
Nitrobenzene	+56.2 [11]	−22.4 [7]	8.3 [8]	+1.2 [11]
m-xylene	+67.3 [11]	−30.6 [7]	10.1 [8]	−1.8 [11]

* Author's calculations

The temperature coefficient of the velocity of sound,

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_p = \left(2 - \frac{V}{T_s}\right)\alpha\,\frac{1}{2},$$

is, as can be seen, expressed exclusively by a change in the volume. This fact should be stressed since, from a formal computation of the value

$$\frac{1}{w}\left(\frac{\partial w}{\partial T}\right)_p = \left[\alpha - \frac{1}{\beta}\left(\frac{\partial\beta}{\partial T}\right)_p\right]\frac{1}{2}$$

(see Table 1), some workers conclude that a change in the coefficient of compressibility primarily accounts for the temperature change of the sound velocity. If the intermolecular compressibility is to be considered as a real measure of the elastic properties, it can be easily seen that almost the only reason for a temperature dependent sound velocity at a constant pressure is the change in volume.

4. In conclusion it can be said that if we consider only the effect of the temperature dependent change in volume at constant pressure, then we obtain:

(a) good agreement, as regards the sign and the absolute value, of the "measured" temperature coefficient of the liquid compressibility (³),

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(³) In view of the slight difference in the numerical values of the ratio V_s/V obtained by different various methods the estimates presented above do not at present permit the isothermal and adiabatic compressibilities (cf. Table 1) to be descerned.

(b) good agreement, as regards the sign and the absolute value, of the temperature coefficient of the sound velocity, and that

(c) it can be accepted to a good approximation over the whole range of the liquid state that the intermolecular compressibility changes only very slightly with temperature, at constant pressure. The change in the "measured" compressibility is simulated by a change of volume.

The conclusions (a), (b) and (c) result from the assumption that the intermolecular compressibility of a liquid consists of a kinetic compressibility, which is independent of temperature at constant pressure, and of a potential compressibility which is considerably lower than the kinetic compressibility.

The relation between the velocity of the thermal translational motion of the molecules in a liquid and the sound velocity is more complex than the similar relation for perfect gases. The considerations presented in this paper are thus the first approximation of the dependencies between these quantities which as yet are undetermined.

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Received on April 8th, 1977

ARCHIVES OF ACOUSTICS
3, 1, 57-66 (1978)

ON AN ACOUSTIC METHOD FOR THE DETERMINATION OF THE DENSITY OF A LIQUID AS A FUNCTION OF PRESSURE

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On the basis of Schaaffs paper and Grüneisen's theory it has been shown that the Rao expression at constant temperature does not depend on the pressure. It results from the stability of the Rao-Schaaffs expression that it is possible to determine the density of a liquid as a function of pressure by the intermediary of quantities measured exclusively under normal pressure. The method provides a better agreement of the calculated values with experimental ones than do other methods.

1. Introduction

A precise determination of the density of a liquid as a function of the temperature T and the pressure p can be reduced to the hitherto unsolved problem of the liquid state equation. Although there exist many empirical or semi-empirical liquid state equations, none of these permits determination of the volume (or the density) with satisfactory accuracy over broad intervals of pressures and temperatures. In addition, these equations are predominantly specific rather than universal.

The generally valid thermodynamical differential equations do not help in solving the problem since the values of the partial derivatives of the parameters of the liquid state are unknown. Thus resort must be made, with the present state of knowlegde, to the semi-empirical equations. The choice of an equation is purely arbitrary and depends, for example, on the kind of liquid and the relevant interval of temperatures and pressures. The determination of the relationship $V = V(p, T)$ in extreme conditions now assumes a special importance with a view to the operating conditions of engine fuels and lubricants in aviation and rocket technology.

It should be noted that **Wehr** [1] and **Szachnowski** [2] have, for a long time been engaged in the problem of the determination of the density of a liquid as a function of the pressure. For various aviation fuels and oils they have succeeded in achieving satisfactory agreement with experimental results by assuming that the ratio of the specific heats in pressure intervals of the order of several hundred atmospheres is constant. Such an assumption is not valid for greater pressure changes and thus the continuation of the work started by WEHR is not possible. The theoretical solution of the problem of the dependence of $\varkappa$ on the pressure is not possible with the knowledge available(1), while the experimental material regarding this problem is very poor.

In this situation it has been decided to resume work on the determination of the density of a liquid as a function of pressure, but with an acoustic method, because of the high efficiency and accuracy of present-day ultrasonic measurement techniques. The starting point is the empirical fact stated recently by SCHAAFFS that the so-called Rao expression — which has so far been investigated at constant atmospheric pressure as a function of temperature — has proved to be independent of the pressure for a constant temperature.

2. The independence of Rao's formulation from the pressure

Using the results of measurements of sound velocity and density made by RAJAGOPALAN, CARNEVAL and LITOVITZ for *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and *n*-dodecane, and for methyl, ethyl, propyl and *n*-butyl alcohols, as well as the results obtained by VEDAM and HOLTON for water, SCHAAFFS has stated that the so-called Rao expression is essentially independent of pressure, especially for pressures above 1000 atm.

Some results of his calculations are given in Table 1. The measurements were made at a temperature of 20°C.

Table 1

Substance	p [atm]	$R_p \times 10^{-3}$ [$\mathrm{cm}^{10/3}\mathrm{s}^{-1/3}\mathrm{mol}^{-1}$]	Substance	p [atm]	$P_p \times 10^{-3}$ [$\mathrm{cm}^{10/3}\mathrm{s}^{-1/3}\mathrm{mol}^{-1}$]
n-heptane	1	7.13	*n*-dodecane	1	11.50
	785	7.32		785	11.80
	1370	7.36		1370	11.90
Methyl alcohol	1	1.943	ethyl alcohol	1	2.85
	1000	2.012		1000	2.95
	2000	2.022		2000	2.96
n-propyl alcohol	1	3.670	*n*-octane	1	8.00
	3000	3.870			
	8000	3.915		785	8.21
	10000	3.925		1370	8.28

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(1) Thermodynamics provides no temperature and pressure dependence of the specific heat and no such relation should be expected to be stated since the material constants are a consideration of importance. The situation is identical to that for the problem of the liquid state equation. Thermodynamics is not capable of providing such an equation (C. SCHÄFER, *Introduction to theoretical physics*, vol. II).

Schaaffs [3] was investigating the expression

$$R_p = w^{1/3}\left(\frac{M}{\varrho}\right),$$

where w is the sound velocity, ϱ is the liquid density and M is the molar mass.

However, it is known that in the range of variable temperatures and constant pressures more exact results are obtained by using, for the determination of various molecular quantities, the individual power exponent according to Kuczera [4, 5, 6]. An attempt has therefore been made to investigate the dependence of the Rao expression by using the individual value of the power exponent determined for normal pressure.

In the calculations use has been made of the results of measurements of the sound velocity and the density for *n*-pentane over a pressure range from 1 to 8000 atm, contained in the papers by Ikramow and Bieliński [7].

The results of these calculations are presented in Table 2.

Table 2

Δp [atm]	$R_p \times 10^{+4}$	Remarks
0	13.4	
500	13.8	1. Measurements were made at a temperature of 20°C
1000	13.8	
1500	13.7	2. The maximum error R_p is ±1.5 %
2000	13.8	
2500	13.8	3. In the calculations the individual power exponent has
3000	13.8	been used
3500	13.8	$q = 2.83$
4000	13.9	
4500	13.8	
5000	13.9	$q = \dfrac{\dfrac{1}{w}\left(\dfrac{\partial w}{\partial T}\right)_{p_1}}{\dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_{p_1}}$
5500	13.8	
6000	13.8	
6500	13.8	p_1 = normal pressure
7000	13.8	
8000	13.9	

It can be seen that the application of an individual exponent gives a better stability of the expression $R_p = w^{1/q}(M/\varrho)$ with changing pressure and constant temperature.

Accidental deviations are the result of errors made during the measurement. Worthy of note, although so far unexplained, is the fact that for all high pressures the exponent q has remained unchanged.

3. An attempt to explain the independence of the Rao expression from the pressure

Let us consider, following GRÜNEISEN [8] and others, the liquid molecules as point sources of force arranged momentarily along a certain direction at distances $\bar{r}$ and bonded by intermolecular forces. When a molecule is shifted by ξ, then the force of the interaction of two nearest molecules is $f \approx 2\xi f'(\bar{r})$. Let us assume that neighbouring molecules are distributed evenly on spheres of radii $S_i\bar{r}$. The force of interaction from the neighbours distributed along a certain considered direction is $2\xi \sum_i (S_i \bar{r})$. If we denote $\frac{1}{2}\cos^2\varphi_i = t_i$, where φ_i are the angles to the chosen direction, then the force of interaction from all the neighbours will be $f = 2\xi \sum_i t_i f'(S_i\bar{r})$.

The potential of the interaction is expressed by equation

$$\varphi(r) = -\frac{\alpha}{r^x} + \frac{\beta}{r^y}, \tag{1}$$

where x and y are constants ($y > x$), and α and β are individual constants.

In considering equation (1), the directing force D is

$$D = \frac{f}{\xi} = 2\left\{y(y+1)\frac{\beta}{\bar{r}^{y+2}}\sum_i \frac{t_i}{S_i^{y+2}} - x(x+1)\frac{\alpha}{\bar{r}^{x+2}}\sum_i \frac{t_i}{S_i^{x+2}}\right\}. \tag{2}$$

We write

$$\left(\sum_i \frac{p_i}{S_i^x}\right)\alpha = a \quad \text{and} \quad \left(\sum_i \frac{p_i}{S_i^y}\right)\beta = b,$$

where p_i is the number of neighbours as a distance $S_i\bar{r}$.

It should be noted that in the equilibrium state

$$\frac{ax}{\bar{r}_0^{x+1}} = \frac{by}{\bar{r}_0^{y+1}}.$$

Then

$$D = 2\frac{ax}{\bar{r}^{x+2}}\left\{\left(\frac{\bar{r}_0}{\bar{r}}\right)^{y-x}(y+1)\Psi(y) - (x+1)\Psi(x)\right\}, \tag{3}$$

where

$$\Psi(y) = \frac{\sum_i \frac{t_i}{S_i^{y+2}}}{\sum_i \frac{p_i}{S_i^y}} \quad \text{and} \quad \Psi(x) = \frac{\sum_i \frac{t_i}{S_i^{x+2}}}{\sum_i \frac{p_i}{S_i^x}}.$$

Let us derive the GRÜNEISEN factor $\gamma = d\ln\nu / d\ln v$, which as GRÜNEISEN has proved experimentally, does not depend on the temperature and pressure.

Since the frequency of vibration of the molecules ν, assuming a monochromatic vibration spectrum, is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{D}{\mu}},$$

we have

$$d(\ln\nu) = \frac{1}{2}\,d(\ln D) \qquad \text{and}\; v = \text{const}\,\bar{r}^3,$$

where D is the directing force, and μ the oscillator mass, so $d(\ln v) = 3\;d(\ln\bar{r})$. Consequently,

$$\gamma = -\frac{d(\ln\nu)}{d(\ln v)} = -\frac{1}{6}\,\frac{d(\ln D)}{d(\ln\bar{r})}. \tag{4}$$

If we assume $\bar{r}_0 \approx \bar{r}$ (the increase of temperature will indeed cause an increment in $\bar{r}$, but the increase in pressure will reduce this increment in $\bar{r}$), it can be shown that

$$\gamma = \frac{1}{6}\,\frac{(y+2)(y+1)\Psi(y) - (x+2)(x+1)\Psi(x)}{(y+1)\Psi(y) - (x+1)\Psi(x)}. \tag{5}$$

If we take into consideration the interaction of all the more distant neighbours, then $\Psi(x) \approx 0$ and $\Psi(y) \approx 1/9$. Consequently,

$$\gamma = \frac{1}{6}(y+2). \tag{6}$$

According to BORN-KÁRMÁN the velocity of wave propagation is expressed by the formula

$$w = r\sqrt{\frac{D}{\mu}} = 2\pi r\nu_m.\text{(2)} \tag{7}$$

Since

$$r = \sqrt[3]{\frac{v}{kN_A}},$$

where v denotes the molar volume, k is the structural factor, which is independent of pressure and temperature, and N_A is the Avogadro number, hence after logarithmic differentiation we obtain

$$d(\ln w) = \tfrac{1}{3}d(\ln v) + d(\ln\nu_m),$$

i.e.

$$\frac{d(\ln w)}{d(\ln v)} = \frac{1}{3} + \frac{d(\ln\nu_m)}{d(\ln v)}. \tag{8}$$

---

(2) According to Eucken, for normal monochromatic body the limiting frequency of the spectrum is $\nu_m \approx \nu$.

Substituting equation (6) into equation (8), we obtain

$$\frac{d(\ln w)}{d(\ln v)} = \frac{1}{3} - \frac{1}{6}(y+2) = -\frac{y}{6}$$

or

$$\frac{\frac{1}{w}\left(\frac{\partial w}{\partial p}\right)_T}{\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T} = -\frac{y}{6} = -q. \tag{9}$$

In integral form, expression (9) becomes

$$w^{1/q}\left(\frac{M}{\varrho}\right) = R_p = \text{const}. \tag{10}$$

In this manner we obtain the analogue of Rao's expression which is valid for $T = \text{const}$, as distinct from the classical rule which can be applied for $p_i = \text{const}$ with a universal power exponent $q = 3$. Expression (10) is certainly an approximate form of more complex, but as yet unknown relations between the sound velocity and the liquid volume.

4. Consequences of the Rao-Schaaffs rule

It will be demonstrated that, from the stability of the Rao-Schaaffs expression, it is possible to determine the liquid density as a function of pressure using quantities measured exclusively under normal conditions.

For this purpose we may observe that

$$w^2 = \left(\frac{\partial p}{\partial \varrho}\right)_s, \tag{11}$$

hence

$$p_1 - p_2 = \int\limits_{\varrho_1}^{\varrho_p} w^2 \partial \varrho,$$

where ϱ_1 denotes the density at pressure p_1, and ϱ_p is the density at pressure p.

Since

$$R_p = w_1^{1/q}\left(\frac{M}{\varrho_1}\right) = w^{1/q}\left(\frac{M}{\varrho}\right), \tag{10'}$$

the substitution of equation (10′) into equation (11) and subsequent integration imply

$$p - p_1 = \frac{w_1^2 \varrho_1}{2q+1}\left[\left(\frac{\varrho_p}{\varrho_1}\right)^{2q+1} - 1\right]. \tag{12}$$

From (12) it is possible to determine the density ϱ_p as

$$\varrho_p = \varrho_1 \sqrt[2q+1]{(2q+1)\frac{p-p_1}{w_1^2 \varrho_1} + 1}. \tag{13}$$

It can be seen that in formula (13) there are only the quantities measured at normal pressure.

When we assume $q = 3$ (3) a universal power exponent in expression (10′), equation (13) takes the form

$$\varrho_p = \varrho_1 \sqrt[7]{\frac{7(p - p_1)}{w_1^2 \varrho_1} + 1}. \tag{13a}$$

If we neglect the pressure p_1, as being considerably smaller than p, then equation (12) can be written in the form

$$p = \frac{1}{7} w_1^2 \varrho_1 \left[\left(\frac{\varrho_p}{\varrho_1} \right)^7 - 1 \right]. \tag{12a}$$

Kirkwood [9] obtained an analogous equation empirically in the form

$$p = B(S) \left[\left(\frac{\varrho_p}{\varrho_1} \right)^n - 1 \right], \tag{14}$$

where $B(S)$ and n are constants for a given liquid.

Equation (14) applies well for water within the range of pressures from 1 to 25000 atm for $n = 7.15$.

Taking advantage of relation (13), the density has been calculated for n-heptane and for diethyl ether over a broad range of pressures and at ambient temperature. The results have been compared with experimental data. Results of these calculations are shown in Tables 3 and 4.

Table 3. The calculation of the density of n-pentane at a temperature of 20°C

p [atm]	ϱ_{table} [g/cm³]	$\varrho_{\text{calculated}}$ Eq. (13a)	Deviation [%]	$\varrho_{\text{calculated}}$ Eq. (13)	Deviation [%]	Remarks
1	0.6254	—	—	—	—	1. In formula (13a) the exponent $q = 3$ has been used
500	0.6660	0.664	−0.30	0.665	−0.15	
1000	0.7044	0.693	−1.62	0.695	−1.28	
1500	0.7300	0.715	−2.05	0.717	−1.79	
2000	0.7468	0.734	−1.71	0.738	−1.18	2. In formula (13) the individual exponent $q = 2.832$ is taken according to the data from the tables of Landolt-Börnstein
2500	0.7630	0.751	−1.57	0.755	−1.05	
3000	0.7774	0.765	−1.59	0.770	−0.95	
3500	0.7910	0.778	−1.64	0.784	−0.88	
4000	0.7996	0.790	−1.20	0.797	−0.33	
4500	0.8110	0.801	−1.23	0.808	−0.37	
5000	0.8195	0.811	−1.04	0.819	−0.06	
5500	0.8300	0.821	−1.08	0.829	−0.12	3. Tabulated values of the density are the average value of the measurements by Bielinski and Bridgeman
6000	0.8385	0.829	−1.13	0.839	+0.06	
7000	0.8535	0.845	−1.00	0.856	+0.29	
8000	0.8669	0.860	−0.80	0.871	+0.47	

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(3) The average value for liquid n-paraffins from C_5 to C_{16} is 2.941, whereas the average value for a series of homological paraffins, olefins as well as aromatic hydrocarbons is $q = 2.963$ [13].

Table 4. Calculations of

Δp [bar]	ϱ_{table}	*n*-heptane $\varrho_{\text{calculated}}$ [g/cm³]	Deviation [%]	Remarks
0	0.6753	—	—	For the calculations the exponent $q = 2.953$ is taken according to Landolt's table $w = 1113\left[\frac{\text{m}}{\text{s}}\right]$ $\frac{dw}{dT} = -4.14\left[\frac{\text{m}}{\text{s deg}}\right]$ $\alpha = 12.60\cdot 10^{-4}$ [deg^{-1}] for a temperature +30°C. The values of density are from Wargaftik [12].
50	0.6803	0.6793	−0.15	
100	0.6849	0.6831	−0.26	
200	0.6933	0.6904	−0.42	
300	0.7010	0.6973	−0.53	
500	0.7142	0.7100	−0.59	
1000	0.7406	0.7369	−0.50	
1500	0.7612	0.7590	−0.29	
2000	0.7783	0.7738	−0.06	
3000	0.8063	0.8090	+0.34	
5000	0.8480	0.8558	+0.92	

It can be seen from Table 3 that better agreement with the experiment is obtained by using the individual exponent q in formula (13), than — the universal exponent $q = 3$ in formula (13a). In further calculations the former will thus be used.

Obviously, in the first approximation it is possible by using the universal exponent $q = 3$, to determine the liquid density at higher pressures with an accuracy of 2-3 %, and this requires knowlegde of the liquid density and the sound velocity for only one measuring point, e.g. at room temperature and normal pressure.

It should be added that even better agreement of the experimental results with the values of the densities calculated on the basis of formula (13) can be obtained with the aid of experimental data on the liquid density and sound velocity at a higher pressure than that of the normal pressure (13).

As an example, assuming as initial data for the calculations for diethyl ether at a pressure of $p = 500$ atm $\varrho = 0.7615$ g/cm³ (from BRIDGEMAN [11]), and $w = 1284$ m/s (according to RICHARDSON and TAIT [10]), then the average deviation of the results of the values of the densities calculated from experimental data obtained by BRIDGEMAN [11] in the pressure range from 1000 to 12 000 atm is ±0.25 %, compared to a deviation of ±0.69 % for initial data taken at normal pressure. Thus, it is possible in some cases to extrapolate the results obtained at not too high pressures to considerably higher pressure ranges.

5. Results

The value of the so called Rao expression at constant temperature is almost independent of the pressure, as was pointed out by SCHAAFFS. In this paper it density of n-heptane and diethyl ether

p [atm]	ϱ table [g/cm^3]	Diethyl ether ϱ calculated [g/cm^3]	Deviation [%]	Remarks
1	0.7138	—	—	
500	0.7615	0.755	−0.88	For the calculations the exponent value $q = 2.840$ has been taken according to Landolts'table $w = 1006$ [m/s] $\frac{dw}{dT} = 4.66$ [m/s deg] $\alpha = 16.31\quad 10^{-4}$ [deg^{-1}] $t = 20°\mathrm{C}$
1000	0.7885	0.786	−0.30	
1500	0.8117	0.8116	−0.01	
2000	0.8319	0.833	+0.16	
2500	0.8498	0.852	+0.27	
3000	0.8658	0.869	+0.35	
3500	0.8800	0.884	+0.45	
4000	0.8928	0.898	+0.55	
4500	0.9045	0.910	+0.64	
5000	0.9152	0.922	+0.75	
6000	0.9339	0.943	+0.99	Density data are taken from Bridgeman's papers [11]
7000	0.9508	0.962	+1.18	
8000	0.9670	0.979	+1.23	
9000	0.9826	0.994	+1.19	
10000	0.9976	1.008	+1.09	
11000	1.0120	1.022	+0.95	
12000	1.0256	1.034	+0.80	

has been shown that a somewhat better stability of this expression is obtained by using individual liquid exponents and an attempt has been made to prove this fact theoretically.

From this a relation has been obtained from which it is possible to determine the pressure dependence of the liquid density over a broad pressure interval. This method is very simple since it requires only the knowledge of changes in density and sound velocity as a function of temperature at normal pressure and gives better agreement of the calculated densities with experimental values than do the majority of known methods.

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Received on 3rd January 1977

ARCHIVES OF ACOUSTICS
3, 1, 67-70 (1978)

THE VELOCITY OF PROPAGATION AND ATTENUATION OF ULTRASOUND IN METHYLPYRIDINES

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The results of measurements of c and α/f^2 as functions of temperature for five methylpyridines: β- and γ-picolines and 2.4, 2.5 and 3.5 lutidines are given.

1. Introduction

Investigations of the propagation velocity of an ultrasonic wave on α-picoline as a function of temperature [1] have shown that the functional dependence $c(T)$ is linear, but with two regions of linearity. Above 293 K the temperature coefficient of the velocity of ultrasound is -4.9 m $\mathrm{s}^{-1}\mathrm{deg}^{-1}$, but -3.9 below this temperature. This gives evidence for the existance of an additional "phase" transition (of an association-disassociation type or of a defreezing-freezing of the internal motions of the molecules) between the melting and solidification points.

Previous investigations indicated that in other methylpyridines similar transitions should be observed. In the region of the transitions, the liquids should exhibit relaxation properties.

The purpose of this paper is to describe measurements on a number of methylsubstitute pyridines in which relaxation regions might have been found. Measurements were made of the propagation velocity c and the ultrasound attenuation coefficient α as functions of temperature for five compounds: β- and γ-picolines and 2.4, 2.5 and 3.5 — lutidines.

2. Apparatus

The experimental results for c and α were obtained using an ultrasonic phase pulse interferometer type UI12 [2] at a frequency of 12 MHz. Temperature stabilization was maintained by means of a temperature regulator, type 650-UNIPAN with a platinum sensing device type 210 s 3 wire — 100 ohm, to an accuracy ±0.05 K.

3. Results of the measurements

Fig. 1 represents the relationship between the attenuation coefficient divided by the frequency squared and the temperature, over the temperature range 280-330 K for γ-picoline. The value of this coefficient is initially constant and then rises with increasing temperature. For the same liquid the relation between the propagation velocity and the temperature is shown in Fig. 2.

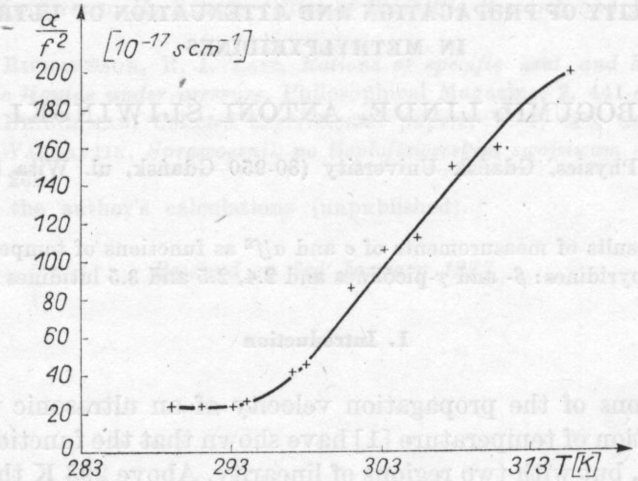

Fig. 1. The dependence of α/f^2 on temperature for γ-picoline at a frequency of 12 MHz

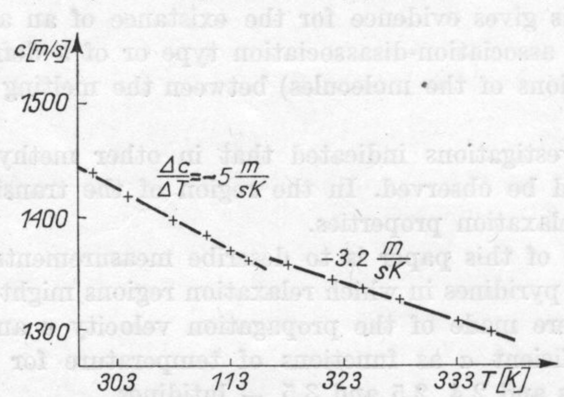

Fig. 2. The dependence of the ultrasonic propagation velocity c, on temperature for γ-picoline at a frequency of 12 MHz (the corresponding temperature coefficients of the ultrasonic velocity are given above the straight segments)

At about 315 K there is a region in which the curve has a marked change of gradient.

Similar results for the temperature dependencies of α/f^2 and c for 2.5 lutidine are shown in Figs. 3 and 4.

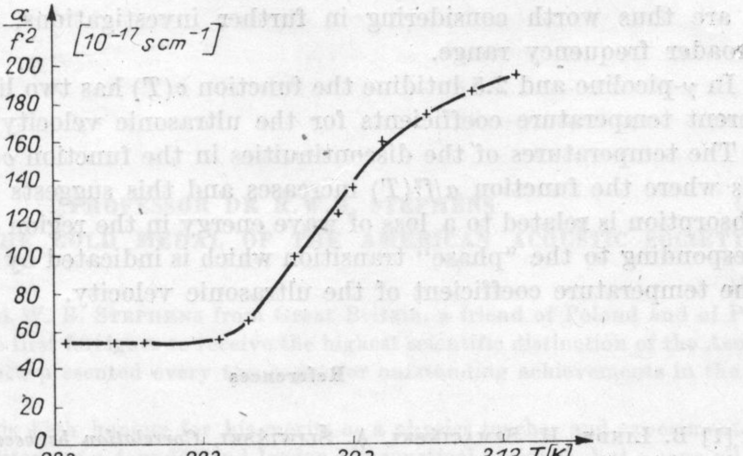

Fig. 3. The dependence of α/f^2 on temperature for 2.5 lutidine at $f = 12$ MHz

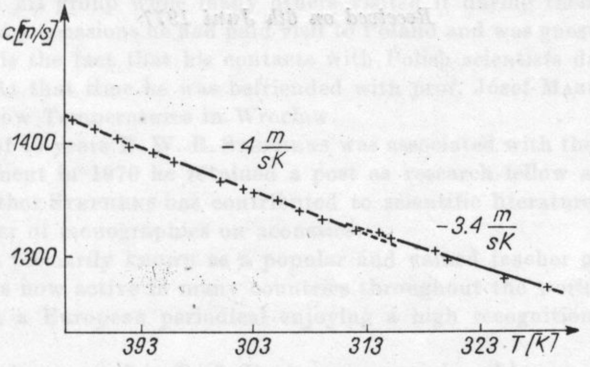

Fig. 4. The dependence of the ultrasonic propagation velocity on temperature for 2.5 lutidine for $f = 12$ MHz (the corresponding temperature coefficients of the ultrasonic velocity are given above the straight segments).

For the other liquids tested no changes in the inclination of the curve $c(T)$ were observed; the velocity coefficients for β-picoline; 2.4 and 2.5 — lutidine being -3.8 ms^{-1} deg^{-1}, -3.7 ms^{-1} and -4.6 ms^{-1} deg^{-1}, respectively.

The measurement errors for the velocity of ultrasound did not exceed 4 ms^{-1} while that for the attenuation coefficient was no more than 5 %.

4. Discussion and results

For all the above-mentioned liquids the graphical representation of the function $\alpha/f^2(T)$ indicates the existence of a relaxation region (for γ-picoline and 2.5 lutidine the representations are shown in Figs. 1 and 3). These dependencies are thus worth considering in further investigations, particularly over a broader frequency range.

In γ-picoline and 2.5 lutidine the function $c(T)$ has two linear ranges, with different temperature coefficients for the ultrasonic velocity (Figs. 2 and 4).

The temperatures of the discontinuities in the function $c(T)$ are in the regions where the function $\alpha/f^2(T)$ increases and this suggests that the increase of absorption is related to a loss of wave energy in the region of the relaxation, corresponding to the "phase" transition which is indicated by the discontinuity in the temperature coefficient of the ultrasonic velocity.

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Received on 6th Juni 1977

CHRONICLE

PROFESSOR DR R.W.B. STEPHENS
AWARDED THE GOLD MEDAL OF THE AMERICAN ACOUSTIC SOCIETY

Prof. Raymond W. B. Stephens from Great Britain, a friend of Poland and of Polish acousticians, was the first foreigner to receive the highest scientific distinction of the Acoustical Society of America presented every two years for outstanding achievements in the field of acoustics.

He received this high honour for his merits as a physics teacher and experimentalist, as an author and editor; as a founder and leader of acoustical societies, but above all as a research supervisor who has taught and inspired a generation of acoustics students.

Prof. R. W. B. Stephens, who for many years had been in charge of an acoustic group at the Imperial College in London, always took care of Polish acousticians of whom a number worked in his group while many others visited it during their scientific stay in Great Britain. On many occasions he had paid visit to Poland and was guest of Polish acousticians. Little known is the fact that his contacts with Polish scientists date as far back as the World War II. At that time he was befriended with prof. Józef Mazur, the late leader of the Institute of Low Temperatures in Wrocław.

Over a period of 45 years R. W. B. Stephens was associated with the Imperial College. Following his retirement in 1970 he retained a post as research fellow at Chelsea College. As the editor and author Stephens has contributed to scientific literature in several journal articles and a number of monographies on acoustics.

However, he is primarily known as a popular and valued teacher of the whole generation of acousticians now active in many countries throughout the world. He is also a co-editor of Acoustica, a European periodical enjoying a high recognition in the milieu of acousticians.

We are glad and congratulate Prof. Stephens in receiving this new award.

Jerzy K. Zieniuk (*Warszawa*)

THE SECOND CONGRESS OF THE FEDERATION OF ACOUSTICAL SOCIETJES OF EUROPE FASE—78

Warszawa, 18—22. IX. 1978

The Federation of Acoustical Societies of Europe has decided that the Second FASE-Congress will be held in Poland.

The Congress is to be organized by the Acoustical Committee of the Polish Academy of Sciences and the Polish Acoustical Society in collaboration with the Institute of Fundamental Technological Research (IPPT – PAN).

The Congress will be held in the conference rooms of the Palace of Culture and Science located in the centre of Warsaw. It will start on Monday 18th September 1978.

The scientific programme will cover the following subjects:

1. **Acoustic waves and the structure of matter**
   molecular acoustics of fluids
   acoustical investigation of the physical properties of solids
   acoustics of inhomogeneous media
2. **Ultrasonic methods of location and recognition**
   nondestructive testing
   medical diagnostics
   geological prospection
   hydroacoustics
3. **Objective and subjective evaluation of sound in a limited space**
   concert halls and auditoria
   industrial halls
   urban areas

There will be plenare sessions, round table discussions and three parallel technical sessions, with the following forms of paper presentation being foreseen: invited lectures, contribution papers, verbal presentation, poster form presentation.

Authors willing to present their papers in poster form will have 5 minutes to present their work during the session for contributed papers. Subsequently they will stay half-an-hour at their displays (booths of area about 4 m^2) to present the paper and discuss details with any interested participants. The materials for presentation may include figures, diagrams, photographs, numerical data, fragments of text etc.

The manufacturers of research equipment will have good opportunities and facilities for presenting their products. Companies interested in exhibiting are kindly requested to write to the Organizing Committee.

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