Fine structure of the Rayleigh line wing and the propagation of transverse hypersound in liquids

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The temperature dependence of the separation of the fine-structure components of the Rayleigh line wing has been studied experimentally in liquid salol and benzophenone. The temperature dependence of the two anisotropy relaxation times, the shear modulus, the ratio of the integrated intensities of the near and further portions of the Rayleigh line wing, and other parameters have also been determined for the same liquids. The use of these data and the formulas of phenomenological theory [14,15] allow us to calculate the separation of the components of the wing fine structure. Satisfactory agreement is observed between the measured and the calculated values. The results allow us to analyze the problem of the propagation of transverse hypersound in liquids.

1. INTRODUCTION

The discovery of the fine structure of the Rayleigh line wing[1] has produced a number of experimental[2-12] and theoretical[13-26] studies of the nature of this phenomenon. The phenomenon of the wing fine structure consists of observation of a doublet in the spectrum of light scattered at an angle ϑ that is different from zero and 180° at definite polarizations of the exciting and scattered light, the separation of the components of the doublet amounts to $(2-6)\times 10^{-2}$ cm^{-1}.

In our first paper,[1] the new phenomenon was explained by proposing that the light scattered as a consequence of anisotropy fluctuations connected with the fluctuations of the shear deformations is modulated by the corresponding Fourier component of the shear deformation. Such an interpretation is confirmed by the polarization properties of the scattered light, by the dependence of the separation of the components of the doublet $2\Delta\nu_m$ on the scattering angle ϑ, and by the dependence of the quantity $2\Delta\nu_m$ on the wavelength of the exciting light. However, some features of the phenomenon were observed which could not be explained by the then existing theories and models.

First of all, it was surprising that the wing fine structure is observed in liquids with a viscosity $\sim 10^{-2}$ poise (P), when, as was thought, only a purely viscous wave exists, such as cannot cause the shifted components. Further, the temperature dependence of the separation of the doublet components turned out to be unusual.[4,8] Upon an increase in the viscosity, the separation of the components $2\Delta\nu_m$ decreases and at a viscosity $\sim 10^{-1}-1$ P, they become unresolvable. The components of the wing fine structure are also not resolved at viscosities less than 10^{-2} P. We shall call this range of the temperature dependence of $2\Delta\nu_m$ the high-temperature branch. At a viscosity $\sim 10^{2}$ P or higher, a triplet appears in the spectrum of the scattered light, and the separation between the shifted components increases with the viscosity; for very viscous liquids, this increase is slowed down (salol). We shall call this region of the variation of the position of the shifted components as a function of the viscosity (temperature) the low-temperature branch.

Thus there emerges a complicated picture of the phenomenon; it was explained qualitatively by the introduction of at least two anisotropy relaxation times.[4] In the low-temperature branch, the dependence of the component shifts on the temperature is described by the Leontovich theory.[27] The behavior of the components of the wing fine structure in the high-temperature branch and the very fact of their existence have been described by none of the theories; the character of the transition from one branch to the other has also remained unclear. Several investigations have now been published which relate to the interpretation of the high-temperature branch only,[13,16,18-26] and the phenomenological theory of Rytov, which pertains to quantitative description of the entire picture of the phenomenon as a whole has appeared. Therefore we shall use precisely this theory to discuss the results of our experimental investigation. Comparisons of experimental results for the high-temperature branch with certain molecular theories have been given in the works of Enright, Stegeman and Stoicheff,[10] Chung and Yip,[19] and Anderson and Pecora.[20]

For calculation of $\Delta\nu_m$ from the equations of the Rytov theory in the temperature range (the viscosity changed from $\sim 10^{-2}$ to $\sim 10^{5}$ P) in which the temperature kinetics of both branches were studied, the parameters entering into the formulas of the theory were determined from independent experiments. Such a calculation opens the way to rather full discussion of the subject phenomenon and explains at least some of its features that have not been understood to date.

In Sec. 2, we shall give the fundamental formulas of the theory, which are written in a form suitable for our purposes, along with the necessary discussion of their physical content, including also the acoustical aspect of this problem.

In Sec. 3 reports measurements of the temperature dependence of the parameters needed for calculation of $\Delta\nu_m$. Section 4 discusses the character of the temperature dependence of the separation of the components of the wing fine structure, and in Sec. 5 we consider the problem of the propagation of transverse sound waves in liquids.

2. FUNDAMENTAL FORMULAS OF THE THEORY AND THEIR DISCUSSION

It follows from the Rytov theory[14,15] that if the process of resorption of anisotropy fluctuations can be described with the aid of two relaxation times τ_1 and τ_2

(arguments will be given below in favor of such an assumption), then the intensity distribution in the polarized components I_{zH} and I_{yz}, in which the wing fine structure is observed, is determined by the expression$^{1)}$

$$I_{zH}=I_{yz}=$$
$$=\frac{kT}{\pi}\varepsilon^2M^2\left\{\frac{R\eta\omega^2}{\omega^2+(\omega^2T_\tau-R\eta q^2/\rho)^2}\cos^2\frac{\vartheta}{2}\left[L_1+2L_2\tau_1\frac{\tau_2}{\tau_M}\left(R\frac{\eta}{\rho}q^2-\omega^2T_\tau\right)\right]\right.$$
$$\left.-\frac{R\eta}{1+\omega^2T_\tau^2}\cos^2\frac{\vartheta}{2}\left(L_1-2L_2\omega^2T_\tau\tau_1\frac{\tau_2}{\tau_M}\right)\right\}+I_W. \tag{1}$$

The intensity distribution in I_{yH} has the form$^{2)}$

$$I_W=I_{yH}=\frac{kT}{4\pi}\frac{(2\varepsilon M\eta-X_\infty\tau_2)^2}{\mu_\infty(\tau_1-\tau_2)(\tau_M-\tau_2)}\left\{\frac{\tau_1}{1+\omega^2\tau_1^2}+\frac{1}{D}\frac{\tau_2}{1+\omega^2\tau_2^2}\right\}. \tag{2}$$

In (1) and (2), ω is the frequency reckoned from the frequency ω_0 of the exciting light, $\epsilon = n^2$, ρ, η, and M are respectively the dielectric constant, the density, the viscosity and the Maxwell constant; X_∞ and μ_∞ are the limiting values of the elasto-optic constant and the shear modulus as $\omega \to \infty$,

$$\tau_M=\frac{\eta}{\mu_\infty},\quad q=2n\frac{\omega_0}{c}\sin\frac{\vartheta}{2}.$$

In (1) and (2) we have introduced the abbreviations

$$T_\tau=\tau_1\frac{1-\tau_2/\tau_M+\tau_2/\tau_1+\omega^2\tau_2^2\tau_1/\tau_M}{1+\omega^2\tau_1\tau_2(\tau_1-\tau_M+\tau_2)/\tau_M}, \tag{3a}$$

$$R=\frac{1+\omega^2\tau_1^2\tau_2^2/\tau_M^2}{1+\omega^2\tau_1\tau_2(\tau_1-\tau_M+\tau_2)/\tau_M}, \tag{3b}$$

$$L_1=\frac{(1+\omega^2\tau_1\tau_3\tau_2/{}_M)^2-\omega^2\tau_1^2(\tau_2/\tau_M-\tau_3/\tau_1)^2}{(1+\omega^2\tau_1^2\tau_2^2/\tau_M^2)^2}, \tag{3c}$$

$$L_2=\frac{(1-\tau_3\tau_M/\tau_1\tau_2)(1+\omega^2\tau_1\tau_3\tau_2/\tau_M)}{(1+\omega^2\tau_1^2\tau_2^2/\tau_M^2)^2}, \tag{3d}$$

$$D=\frac{\tau_1-\tau_M}{\tau_M-\tau_2}\left(\frac{2\varepsilon M\eta-X_\infty\tau_2}{X_\infty\tau_1-2\varepsilon M\eta}\right)^2 \tag{4}$$

and $\tau_3 = X_\infty\tau_1\tau_2/2\epsilon M\eta$. It follows from (2) that D (expression (4)) gives the ratio of the integrated intensities of the part of the wing whose half-width is $2\delta\omega_1 = 2/\tau_1$ and the part of the wing whose half-width is equal to $2\delta\omega_2 = 2/\tau_2$.

Thus, if η, τ_1, τ_2, τ_M (or μ_∞), M, and D are known, then expressions (1) and (2) can be used to calculate the spectrum of scattered light and we can find X_∞ from (4).

In the particular case when $\tau_2 = 0$, Eq. (1) goes over at $\vartheta = 90°$ into an expression that is similar in form to that previously obtained by Leontovich:[27]

$$I_{zx}=I_{yx}=\frac{kT}{2\pi}\frac{\varepsilon^2M^2\eta}{\tau_1}\left\{\frac{\omega^2\tau_1}{\omega^2+(\Omega_m^2-\omega^2)^2\tau_1^2}+\frac{\tau_1}{1+\omega^2\tau_1^2}\right\}, \tag{5}$$
$$\Omega_m^2=\eta q^2/\rho\tau_1.$$

The first term in (5), which can be represented in the form of the difference of two Lorentzian contours with real parameters for the case $2\Omega_m\tau_1 < 1$, is responsible for the appearance of the doublet at a frequency $\omega \pm \Omega_m$:

$$I_1\sim\frac{\tau_1}{(1-4\Omega_m^2\tau_1^2)^{1/2}}\left\{\frac{a^2}{a^2+\omega^2}-\frac{b^2}{b^2+\omega^2}\right\};$$
$$a^2,\ b^2={}^1\!/_2[1/\tau_1^2-2\Omega_m^2\pm(1-4\Omega_m^2\tau_1^2)^{1/2}]. \tag{6}$$

The corresponding time correlation function has the form

$$f_1(t)=\frac{1}{\pi}\int_{-\infty}^{\infty}I_1(\omega)\cos\omega t\,d\omega= \tag{7}$$
$$=\begin{cases}\exp(-t/2\tau_1)\{\operatorname{ch}x-(1-4\Omega_m^2\tau_1^2)^{-1/2}\operatorname{sh}x\}, & 2\Omega_m\tau_1<1\\ \exp(-t/2\tau_1)\{\cos x-|1-4\Omega_m^2\tau_1^2|^{-1/2}\sin x\}, & 2\Omega_m\tau_1>1\end{cases}$$

where $x = t|1 - 4\Omega_m^2\tau_1^2|^{1/2}/2\tau_1$. Consequently, for $2\Omega_m\tau_1 > 1$, the time dependence of the Fourier-component of the anisotropy fluctuations has an oscillating character; in the case $2\Omega_m\tau_1 < 1$, it represents the difference in the exponential (but this is not an aperiodic law of variation). For $2\Omega_m\tau_1 \ll 1$, the second term in (5) will give a broad wing in the spectrum, against the background of which the doublet is observed, and for $2\Omega_m\tau_1 \gg 1$ this term gives a central component, and a triplet should be observed in the spectrum.

In the case $\tau_1 \neq \tau_2$ we obtain the following expressions for the velocity V_T and the amplitude absorption coefficient α of the transverse sound[17]

$$\alpha V_T/\omega=(1+\omega^2T_\tau^2)^{1/2}-\omega T_\tau, \tag{8}$$

$$V_T=(2\eta\omega/\rho)^{1/2}[(1+\omega^2T_\tau^2)^{1/2}-\omega T_\tau]^{1/2}K, \tag{9}$$

$$K=\left\{\frac{(1+\omega^2T_\tau^2)[1+\omega^2\tau_1(\tau_1-\tau_M+\tau_2)\tau_2/\tau_M]}{(1+\omega^2\tau_1^2)(1+\omega^2\tau_2^2)}\right\}^{1/2}. \tag{9a}$$

It was shown earlier[17] that for $\tau_1(\tau_M - \tau_2) \gg \tau_M^2 + 6\tau_M\tau_2 + \tau_2^2$ a minimum and a maximum appear on the curve of the dependence of $\alpha v_T/\omega$ on $\omega\eta$ at the frequencies

$$\omega_{min}\approx\tau_1^{-1}(\tau_M/\tau_2)^{1/2},\qquad \omega_{max}\approx\tau_2^{-1}[(\tau_M-\tau_2)/\tau_1]^{1/2}.$$

Here the region where $2\omega T_\tau > 1$ (the oscillatory law of variation of the correlation-function Fourier component) is bounded by the limits $1 < \omega\tau_1 < 4\tau_M/\tau_2$, and also $\omega > 1/\tau_2$. The appearance of the minimum indicated above can mean that at a definite temperature, in the frequency range $\omega \sim \omega_{min}$, the scattered light will be modulated by a weakly damped transverse hypersonic wave, while at somewhat lower and somewhat higher temperatures the hypersonic wave should be strongly damped. Consequently, in each specific case, an analysis is needed as to what situation is realized in practice.

The generally cumbersome expression (1) can be materially simplified when $\tau_1 \gg \tau_M$, $\tau_M \gg \tau_2$ and $\tau_3 \gg 2\tau_2$, and this is just the set of conditions which are satisfied for the materials studied in this paper. Under these conditions, the term with L_2 can be neglected in (1) in the vicinity of the maximum of the components of the doublet. Consequently, in the region of the doublet we can use the formula

$$I_{zH}=I_{yz}=\frac{kT}{\pi}\varepsilon^2M^2RL_1\eta\cos^2\frac{\vartheta}{2}\left\{\frac{\omega^2}{\omega^2+(\omega^2T_\tau-Rq^2\eta/\rho)^2}-\frac{1}{1+\omega^2T_\tau^2}\right\}+I_W. \tag{10}$$

The first term in (10), which describes the doublet, has a maximum at the frequency determined by the condition$^{3)}$[17]

$$\omega^2T_\tau=R\eta q^2/\rho,$$

from which, using (3a) and (3b), we find

$$\omega_m^2=\frac{1}{2}\Omega_T^2\frac{\tau_M}{\tau_1}[-A+(A^2+4\gamma)^{1/2}],$$
$$\Omega_T=\left(\frac{\mu_\infty}{\rho}\right)^{1/2}q,\quad \gamma=(\Omega_T^2\tau_2^2)^{-1},\quad A=\gamma\left(1-\frac{\tau_2}{\tau_M}+\frac{\tau_2}{\tau_1}-\frac{\tau_1}{\gamma\tau_M}\right). \tag{11}$$

Expression (11) can be used to calculate the shift of the components only outside of the region of strong variation of R and L_1.

It follows from (11) that for large γ the shift of the components of the wing fine structure is determined by the expression

$$\omega_m'\approx(\eta/\rho\tau_1)^{1/2}q, \tag{12}$$

and for small γ we have for ω_m

$$\omega_m'' \approx (\eta/\rho\tau_M)^{1/2} q \equiv \Omega_T. \tag{13}$$

The transition from the first case to the second takes place in the temperature range where $\gamma \sim \gamma_{tr}$, and

$$\gamma_{tr} = \frac{\tau_1^2}{\tau_1\tau_M - \tau_1\tau_2 + \tau_2\tau_M} \approx \frac{\tau_1}{\tau_M - \tau_2}. \tag{14}$$

Assuming that we can neglect the frequency dependence of R, T_τ and L_1 near $\omega \approx \omega_m$ in (10), we obtain the condition for an oscillatory regime in the form

$$2\omega_m T_\tau(\omega_m) > 1, \tag{15}$$

where ω_m is determined by expression (11) and $T_\tau(\omega_m)$ is obtained from (3a) for $\omega = \omega_m$. It follows from (15) that the character of the time variation of the corresponding Fourier component of the fluctuations is essentially determined by the quantity τ_1/τ_M. If τ_1/τ_M is not very large ($\tau_1/\tau_M < 16$), then (15) is satisfied at

$$\gamma < \frac{4\zeta^2\tau_1^2}{\tau_2^2} \frac{4\zeta^2\tau_M^2 + \tau_2^2}{4\zeta^3\tau_1\tau_M + \tau_2^2}, \tag{16a}$$

where $\zeta = 1 - \tau_2/\tau_M + \tau_2/\tau_1$. If $\tau_2/\tau_M \ll 1$, the condition

$$2\omega_m'\tau_1 > 1. \tag{16b}$$

follows from (16a) with account of (12).

Thus, at $\tau_1/\tau_M < 16$, the temperature kinetics of the wing fine structure looks like this. At low viscosities ($2\omega_m'\tau_1 < 1$) the doublet is observed; the Fourier components of the fluctuations which produced it do not oscillate, and the corresponding transverse wave is strongly attenuated. When the viscosity reaches a value such that $2\omega_m'\tau_1 \gtrsim 1$, the time variation of the corresponding Fourier-components of the fluctuations becomes oscillatory, the absorption of the corresponding transverse hypersonic waves decreases, and at the same time a central component appears in the spectrum with a half-width ($\sim 2/\tau_1$) comparable with the separation of the components of the wing fine structure. In this region of temperatures, a triplet begins to form and the components of the wing fine structure may not be observed at all. Upon a further increase in the viscosity, a clear triplet should be observed in the region where $2\Omega_T\tau_1 \gg 1$, with the separation between the shifted components $2\omega_m''$.

In the case $\tau_1/\tau_M \gg 16$, the transverse sound is attenuated rather weakly, and an oscillating variation of the Fourier components of the fluctuations occurs in the region of sufficiently low temperatures, where the condition

$$2\sqrt{2}\Omega_T\tau_2 > 1 \tag{17}$$

is satisfied, and also in the range of temperatures determined by the inequality

$$1 < 2\omega_m'\tau_1 < \sqrt{6}\tau_M/\tau_2. \tag{18}$$

We note that in the case considered, $\tau_M \gg \tau_2$, the low-temperature boundary ($\tau_1 \leq \sqrt{3/2}\, \tau_M/\omega_m'\tau_2$) of the region (18) is virtually identical with the transitional region determined by expression (14). Furthermore, the region defined by the expression (18) is actually identical (with accuracy to within a factor $\sim\sqrt{2}$) to the region of the minimum on the curve of the dependence of $\alpha V_T/\omega$ on ω, where $2\omega T_\tau > 1$. Consequently, if a region of temperatures exists where (18) is satisfied, then this region—the interval of existence of the high-temperature branch of the wing fine structure—and the interval of temperatures where the oscillatory regime exists overlap at least partially.

Formulas (16)—(18) are given for the case $\tau_1 \gg \tau_M$ and $\tau_M \gg \tau_2$. In the general case, the corresponding expressions are cumbersome and we shall not give them, since $\tau_1 \gg \tau_M \gg \tau_2$ always for the liquids studied here.

3. EXPERIMENTAL INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF THE PARAMETERS WHICH CHARACTERIZE THE SPECTRUM OF DEPOLARIZED LIGHT SCATTERING[4)]

As follows from the formulas given above, knowledge of the temperature dependence of the six parameters given above (τ_1, τ_2, η, μ_∞, D and M or X_∞) is necessary for calculation of the temperature dependence of the separation between the components of the wing fine structure and establishment of the manner of propagation of transverse hypersound. The temperature dependence of the necessary parameters for liquid salol and benzophenone are given in the present work.

The relaxation times τ_1 and τ_2

The anisotropy relaxation times were measured from the intensity distribution in the Rayleigh line wing in the polarization component I_{yx}. For spectral apparatus, we used Fabry-Perot interferometers with dispersion ranges 1, 2.5, 8.33, 16.7 and 50 cm^{-1}, and also a diffraction spectrograph with a grating having 1800 lines/mm (linear dispersion 3.5 cm^{-1}/mm).

An Ne-He laser of power 20—40 mW, λ = 6328 Å served as the source of the exciting light. The near part of the wing was studied on an interference apparatus with pressure scanning of the spectrum and with recording of the spectrum of the scattered light by photon counters. The far part of the wing was studied on interference apparatus with interferometer dispersion ranges of 8.33, 16.7 and 50 cm^{-1} by a photographic method and with use of a diffraction spectrograph and photoelectric recording of the spectrum. It was thus possible to study the intensity distribution in the Rayleigh line wing over a wide range of frequencies from $\sim 10^{-3}$ to 15—20 cm^{-1}.

On plotting the dependence of 1/I on $(\Delta\nu)^2$ ($\Delta\nu = \omega/2\pi c$ is the frequency reckoned from the frequency of the exciting light) for the Rayleigh line wing in salol and benzophenone, we distinguish two straight-line segments on this graph, that correspond to two relaxation processes with different relaxation times τ_1 and τ_2.[5)] The small relaxation time τ_2 was determined from the slope of the straight-line dependence of 1/I on $(\Delta\nu)^2$ in the far wing of the Rayleigh line.[28,29] The large relaxation time τ_1 was determined from the intensity distribution in the portion of the wing close to the unshifted line, with account of the fact[29] that the apparatus function is well approximated by the Voigt function.

The large relaxation time τ_1 was measured in the temperature range 20—90°C in salol and in the range 30—112°C in benzophenone. Figure 1 gives the dependence of τ_1 on η/T (T is the absolute temperature). A linear dependence is observed, and the mean values[6)] for benzophenone and salol are respectively equal to

$$\eta/\tau_1 T = 1.6\cdot 10^6\ \text{dyn/cm}^2\text{-deg}, \quad \eta/\tau_1 T = 1.1\cdot 10^6\ \text{dyn/cm}^2\text{-deg}.$$

The values of τ_1 calculated from these relations differ from those measured by an average of 7%. We have as-

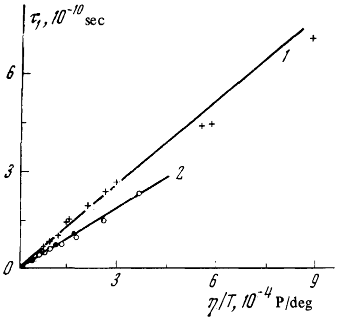

FIG. 1

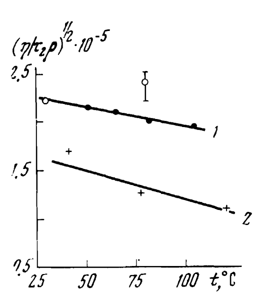

FIG. 2

FIG. 1. Dependence of the anisotropy relaxation time τ_1 on η/T: 1—for salol, 2—for benzophenone; +, o—photoelectric method, ●—photographic method.

FIG. 2. Temperature dependence of $(\eta/\tau_2\rho)^{1/2}$: 1—for benzophenone, 2—for salol; ●, +—measurement by Fabry-Perot interferometer; o—photoelectric measurements by diffraction spectrograph. For benzophenone, the point at t = 30°C was obtained by F. Ganiev (Samarkand State University).

sumed that the relations between τ_1 and η/T given above are also satisfied in the range of low temperatures, where measurements of τ_1 have not been carried out. The values of τ_1 obtained by this method for salol and for benzophenone are given in the Table for the entire temperature range of interest to us.

The small relaxation times, determined from the far wing of the Rayleigh line, were studied in the temperature range 40—120°C in salol and 50—100°C in benzophenone. It was established (Fig. 2) that the value of $(\eta/\tau_2\rho)^{1/2}$ depends linearly, with sufficient accuracy, on the temperature and is equal to

$$(\eta/\tau_2\rho)^{1/2}=(2.36-4.1\cdot 10^{-3}\,t)\cdot 10^5 \text{ cm/sec},$$
$$(\eta/\tau_2\rho)^{1/2}=(1.79-5.8\cdot 10^{-3}\,t)\cdot 10^5 \text{ cm/sec}$$

for benzophenone and salol, respectively (t is the temperature in °C). The accuracy of the measurement of this quantity can be judged by comparison of the interference and diffraction-spectrograph measurements (see Fig. 2). The error in the determination of the value of τ_2 can reach 30% and is connected principally with the fact that the dependences of 1/I on $(\Delta\nu)^2$ are not clearly determined on the graph in the transition region from the near part of the wing to the far part, and from the far part to the region where the inertia of the molecules becomes important.[28,29] Assuming that the dependences of $(\eta/\tau_2\rho)^{1/2}$ thus found can be extrapolated to the region of high viscosities, we have calculated τ_2 for the entire region of temperatures of interest to us (see the Table).

t, °C	ρ, g/cm³	n (λ=6330 Å)	η, cP	$\tau_1\cdot 10^{10}$, sec	$\tau_2\cdot 10^{12}$, sec	$\mu_\infty\cdot 10^{-9}$, dyn/cm²	D
				Salol			
120	1.093	1.556	1.8	0.405	1.4	3.2	1.54
100	1.110	1.558	2.4	0.57	1.5	4.2	1.71
86	1.122	1.564	3.0	0.74	1.6	4.8	1.90
76	1.130	1.570	3.6	0.91	1.75	5.4	2.02
65	1.140	1.573	4.5	1.18	2	6	2.18
46.5	1.155	1.581	7.8	2.16	2.9	7.3	2.47
30	1.169	1.589	17	4.96	5.5	8.6	2.77
20	1.178	1.592	27	8.15	8.2	9.5	2.97
10	1.186	1.597	52	16.3	15	10.2	3.19
—2.5	1.197	1.602	$1.5\cdot 10^2$	55.5	38	11.4	3.49
—9	1.202	1.605	$3\cdot 10^2$	114	74	12.1	3.66
—23	1.214	1.611	$2.4\cdot 10^3$	$8.6\cdot 10^2$	$5.5\cdot 10^2$	13.5	4.1
—40.5	1.229	1.618	$3.5\cdot 10^5$	$1.4\cdot 10^5$	$7\cdot 10^4$	15.3	4.5
—48.5	1.236	1.621	$2.7\cdot 10^7$	$1.1\cdot 10^7$	$5.1\cdot 10^6$	16.5	4.9
				Benzophenone			
112	1.024	1.568	1.52	0.247	0.41	2.7	1.67
96	1.040	1.574	1.9	0.322	0.47	3.4	2.13
90	1.046	1.577	2.1	0.362	0.51	3.7	2.31
74	1.061	1.583	3	0.525	0.67	4.5	2.83
60	1.075	1.589	4.1	0.769	0.86	5.3	3.35
44	1.090	1.595	6.8	1.34	1.3	6.3	4.04
30	1.104	1.601	11	2.27	2.0	7.3	4.75
20	1.114	1.605	17	3.63	2.9	8	5.3
10	1.123	1.609	30	6.6	5.0	8.8	5.9
0	1.133	1.613	65.3	15	10	9.6	6.6
—10	1.143	1.616	$1.4\cdot 10^2$	33	21	10.4	7.4
—23	1.156	1.622	$6.7\cdot 10^2$	$1.7\cdot 10^2$	97	11.6	8.5
—30	1.162	1.624	$2.1\cdot 10^3$	$5.4\cdot 10^2$	$2.9\cdot 10^2$	12.3	9.2
—43.5	1.176	1.630	$6.3\cdot 10^4$	$1.7\cdot 10^4$	$8.3\cdot 10^3$	13.6	10.7
—48.5	1.180	1.632	$4.4\cdot 10^5$	$1.2\cdot 10^6$	$5.7\cdot 10^4$	14.1	11.3

Ratio of the integrated intensities D of the near and far parts of the wing

The ratio of the integrated intensities of the part of the wing near the unshifted line, which is characterized by the large relaxation time τ_1, and the far part of the wing, which is characterized by the small relaxation time τ_2, was measured in benzophenone in the temperature range 51—98°C by Zubkov and Rozhdestvenskiĭ,[7] and in salol in the temperature range 21—72°C by the present authors. For both liquids, this quantity changed by a factor of 2—4 in the temperature interval mentioned.

The quantity $(DT/\rho)^{1/2}$ depends linearly and weakly on the temperature (Fig. 3), and we have, for benzophenone and salol, respectively (in $[\text{deg-cm}^3/\text{g}]^{1/2}$)

$$(DT/\rho)^{1/2}=40-13\cdot 10^{-2}\,t,\qquad (DT/\rho)^{1/2}=28-4\cdot 10^{-2}\,t.$$

We can judge the accuracy of the measurements of D and the above extrapolating expressions for $(DT/\rho)^{1/2}$ from the fact that, in the case of salol, where measurements of different authors are available,[7] the mean deviation of the experimental values of $(DT/\rho)^{1/2}$ from the values calculated from the extrapolation formula does not exceed ~2%.

Limiting value of the shear modulus μ_∞

The temperature dependence of μ_∞ (or $\tau_M = \eta/\mu_\infty$) was determined by extrapolation into the region of the high-temperature branch of the temperature dependence of the velocity of transverse hypersound V_T, which was determined by measurement of the shift $\Delta\nu_T$ of the transverse components at low temperatures. Such extrapolation is made difficult because of the low accuracy of measurement of $\Delta\nu_T$. Since the sound velocity at high viscosity ordinarily depends linearly on the temperature,[28] we have determined the region of temperatures (from the data of[8]) where the velocity of longitudinal hypersound depends linearly on t, and in this region of temperatures, we have drawn a straight line through the

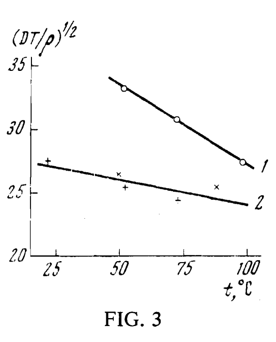

FIG. 3

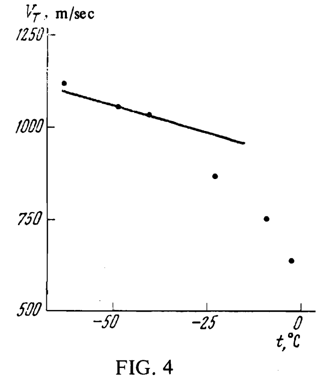

FIG. 4

FIG. 3. Temperature dependence of $(DT/\rho)^{1/2}$: 1—for benzophenone, [7] 2—for salol; +—measurements of the authors, X—measurements of L.

FIG. 4. Temperature dependence of the limiting value of the velocity of transverse hypersound $V_T(\omega\to\infty)$ for salol.

experimental points of the dependence $V_T(t)$ (see, for example, Fig. 4). In this fashion, we obtained for salol and benzophenone, respectively,

$$V_T = 920 - 2.75t \text{ m/sec}, \quad V_T = 920 - 3.6t \text{ m/sec},$$

These expressions for the temperature dependence of V_T were extrapolated into the region of high temperatures and the values of $\mu_\infty = V_T^2\rho$ and τ_M were thus computed for the entire temperature range of interest to us. The calculation shows that even the possible high inaccuracy of the extrapolation of V_T into the region of high temperatures has little effect on the value of the calculated quantity $2\Delta\nu_m$—the separation of the components of the wing fine structure in the high-temperature branch (see Sec. 4 and Fig. 4).

The viscosity and the Maxwell constant M

Measurements of the viscosity were carried out in the temperature range 30—120°C for salol and in the range 40—112°C for benzophenone. In these temperature intervals, the dependence of their viscosities is well expressed by the respective extrapolation formulas

$$\ln\eta = -6.84 + \frac{5.32\cdot 10^2}{T-197}, \quad \ln\eta = -6.86 + \frac{5.26\cdot 10^2}{T-190}$$

(here the viscosity η is expressed in poise). These extrapolation formulas were used to calculate the viscosity in the low-temperature region.

In a wide range of temperatures, the Maxwell constant M for salol has the constant value $M = 2.4 \times 10^{-10}$.[31] For benzophenone, $M = 2.5 \times 10^{-10}$, at t = 55°C was obtained in the measurements of L. V. Smirnova. We used these values in our work.

Thus the temperature dependence of all the parameters necessary for calculation of the shifts of the components of the wing fine structure and the characteristics of propagation of transverse hypersound is now known (see the Table). Calculation of the value of the elasto-optical constant X_∞ is also possible from the relation (4). In the temperature interval −50—120°C, this quantity did not go outside the range 1.6—1.7 for salol or 1.5—1.8 for benzophenone. As a result of the inaccuracy of measurement of the parameters entering into (4) and the weak temperature dependence of X_∞, it is impossible on the basis of our data to draw any definite conclusion as to the sign of dX_∞/dt.

4. TEMPERATURE DEPENDENCE OF THE SHIFT OF THE FINE-STRUCTURE COMPONENTS OF THE RAYLEIGH LINE WING

For computer calculation of the frequency separation of the wing fine structure components $2\Delta\nu_m$ at various temperatures, we used the general formula of the theory (1) and the values of the parameters given in the Table.[8)] For benzophenone, in addition to a calculation using the values of V_T determined from the extrapolation expression $V_T = 920-3.6t$ [m/sec][9)], a calculation was carried out for $V_T = 1200$ m/sec = const. A comparison of the calculation for these two limiting cases of the temperature dependence of V_T (curves 1 and 2, respectively, in Fig. 5) shows that in the high-temperature branch $2\Delta\nu_m$ depends weakly on the value and character of the temperature change of V_T.

It is seen from Fig. 5 that there is not only qualitative, but in a definite temperature range, also quantitative agreement between the experimental results and the calculation. In complete agreement with the results of experiment, the theory gives two branches of the dependence of $2\Delta\nu_m$ on t, while the transition regions from one branch to the other (the region where the wing fine structure is not observed) are the same in both cases.[10)] The same results were also obtained on comparison of the results of calculation with experiment for salol (curve 1 in Fig. 6). However, a more rapid (in comparison with the calculation) temperature change of $2\Delta\nu_m$ is observed for salol and in a certain temperature range there is also a difference between the calculated and measured values.

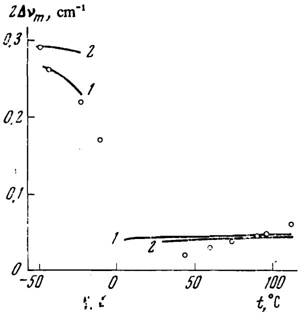

FIG. 5

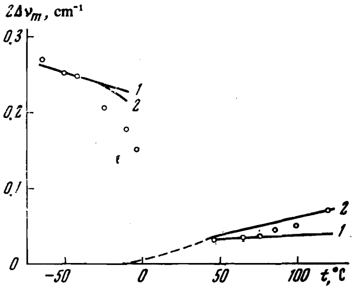

FIG. 6

FIG. 5. Temperature dependence of the separation of the components of the wing fine structure for benzophenone: points—experiment; curve 1—calculation in the case $V_T = 920-3.6t$ [m/sec]; 2—calculation in the case $V_T = 1200$ m/sec.

FIG. 6. Temperature dependence of the separation of the wing fine structure components for salol: points—experiment; curve 1—calculation without account of the effect of the apparatus contour; curve 2—calculation with account of Lorentzian apparatus contour with half-width 2×10^{-2} cm^{-1}.

The curves of Fig. 5 and curve 1 of Fig. 6 were calculated without account of the effect of the apparatus function of the equipment on the positions of the wing fine structure components. In our experiments, the shape of the apparatus function can be approximated by the Voigt function; however, the parameters of this function can change from experiment to experiment. Taking this indeterminacy into account, we selected for the calculation an apparatus contour in the form of the limiting case of a Lorentz distribution with the half width $\Delta\nu_a = 2 \times 10^{-2}$ cm^{-1} that is typical for our setup. This contour was convoluted with Eq. (1) and the maximum of this convolution was found. It is seen from Fig. 6 that for salol, the experimental points on the high-temperature branch lie between curve 2, which was computed with account of the Lorentzian apparatus function, and the curve where the apparatus contour was assumed to be a δ function. The difference between the calculation (curve 2) and experiment, which amounts to 20% on the average, can be attributed to insufficient accuracy in the calculation, associated with the simplifying assumption as to the shape of the apparatus function and the error in the measurement of $2\Delta\nu_m$.

As an illustration of the possible error in measurement of $2\Delta\nu_m$ because of inaccuracy in the identification of the maximum, we have plotted in Fig. 7 the calculated (with account of the Lorentzian apparatus function) temperature dependence of $\Delta\nu_m$ for benzophenone (curve 1) and have also pointed out the region of frequencies (curve 2) where the intensity falls no more than 10% below the intensity at the maximum of the components of the wing fine structure. It is seen from Fig. 7 that, be-

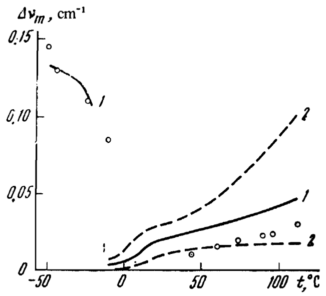

FIG. 7. Temperature dependence of the shift of the wing fine structure components for benzophenone: points—experiment; curve 1—calculation with account of the effect of the apparatus contour; curves 2 bound the region where the intensity in the contour of the wing fine structure differs from the intensity at the maximum by less than 10% (calculated).

cause of the slow falloff of the intensity on both sides of the maximum of the wing fine structure, errors in measurement of the component positions can be very important. Our measurements of the shift of the components of the wing fine structure fall within 10% of the intensity at the maximum.

The entire analysis given here leads to the conclusion that, within the errors of measurement, the formulas of the Rytov theory accurately describe our experimental results over a wide range of the parameters of the medium.[11)]

Actually, the characteristic features of the phenomenon—the existence of two branches of the curve of the shift of the wing fine structure components and the temperature at which the transition occurs from one branch to the other—are in agreement with the conclusions of the theory. If consideration is given the distorting effect of the apparatus function and the possible errors of measurement, satisfactory agreement is also obtained between the calculated and measured values of $2\Delta\nu_m$. Here it must also be pointed out that, as is seen from Figs. 6 and 7, account for the apparatus function in the calculation of $2\Delta\nu_m$ leads to a rather strong but false temperature dependence of this quantity in the high-temperature branch, while such a dependence is practically absent if we neglect the effect of the apparatus contour. Therefore, to resolve the question as to the actual temperature dependence of the shift of the components of the wing fine structure in the high-temperature branch, more complete measurements are necessary than those which have been carried out to date.

5. CHARACTER OF THE PROPAGATION OF TRANSVERSE HYPERSOUND

Using the data of the table and Eqs. (8) and (9), we can calculate the velocity and the absorption coefficient of transverse sound in the studied temperature range for any frequency. For the frequency which corresponds to the frequency of the wing fine structure in the high-temperature branch ($f = 5.4 \times 10^8$ Hz for salol and $f = 6.9 \times 10^8$ Hz for benzophenone), the calculated values of $\alpha\Lambda/2\pi$ for both liquids are shown in Fig. 8. Assuming that the oscillatory law of the time change of the Fourier components of the anisotropy fluctuations develops at $2\omega T_T > 1$ ($\alpha\Lambda/2\pi < 0.62$—this value is indicated by the dashed line in Fig. 8 and subsequent figures), we come to the conclusion that this regime is not realized in the region of the high-temperature branch for the two liquids studied here. But over the entire range of existence of the doublet, for $\omega = \omega_m$, we have $\alpha\Lambda/2\pi < 1$ and, consequently, a transverse wave of such a frequency can be propagated in these media, although its attenuation will be large. In the transition region, where the components of the wing fine structure are not observed, the relation $2\omega_m'\tau_1 \sim 1$ is satisfied. Both these results agree with the theoretical conclusions of Sec. 2 for the case $\tau_1/\tau_M < 16$.

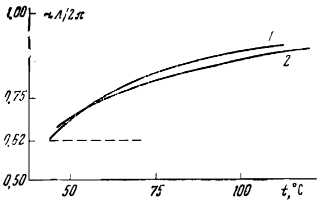

FIG. 8

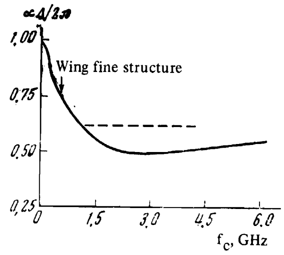

FIG. 9

FIG. 8. Temperature dependence of $\alpha\Lambda/2\pi$ at the frequency of the wing fine structure: 1—benzophenone (f = 0.69 GHz); 2—salol (f = 0.54 GHz).

FIG. 9. Frequency dependence of $\alpha\Lambda/2\pi$ in salol for t = 65°C. The arrow indicates the frequency of the wing fine structure for $\vartheta = 90°$.

Figure 9 shows the calculated frequency dependence of $\alpha\Lambda/2\pi$ for salol at t = 65°C. For this temperature, the frequency corresponding to the positions of the wing fine structure components is one-half the frequency at which $\alpha\Lambda/2\pi = 0.62$. The value of $\alpha\Lambda/2\pi$ at this temperature reaches a minimum $\alpha\Lambda/2\pi \sim 0.5$ at a frequency f = 2.6 GHz, and its maximum, as follows from the expression $\omega_{\max} \approx \tau_2^{-1}[(\tau_M - \tau_2)/\tau_1]^{1/2}$, should be at a frequency f ~ 16 GHz.

The question arises: what are the optimal conditions for experimental observation of the propagation of transverse hypersound by ultrasonic methods in low-viscosity liquids? Equations (8) and (9) and the tabular data allow us to answer question for arbitrary frequencies. Considering that the frequency 0.9GHz has been achieved in real experiments[36,37] and keeping the possible progress in this area in mind, we present the temperature dependence of $\alpha\Lambda/2\pi$ at the frequencies of 0.9 and 3 GHz for salol and benzophenone (Fig. 10). It follows from these data that at f = 0.9 GHz for salol, the minimal[12)] value $(\alpha\Lambda/2\pi)_{\min} = 0.5$ occurs at t = 35°C, and the velocity of the hypersound here should differ from the Newtonian value of the velocity $V_N = (2\eta\omega/\rho)^{1/2}$ by more than 30%. At this same frequency, $(\alpha\Lambda/2\pi)_{\min} = 0.36$ at t = 18°C for benzophenone and the departure of the hypersonic velocity from the Newtonian value will be more than 40%.

For longitudinal hypersound, when its attenuation is small, and on the low-temperature branch of the wing fine structure (high viscosity), the velocity of longitudinal and transverse hypersound can be determined from the shift of ω_m of the corresponding components of the scattered light from the expression $\omega_m = Vq$. However, as follows from a comparison of Eq. (12) with Eq. (8) for V_T, the velocity of transverse hypersound is not directly determined for the high-temperature branch by the factor before q in (12). Consequently, the values of the velocities of transverse hypersound, determined from

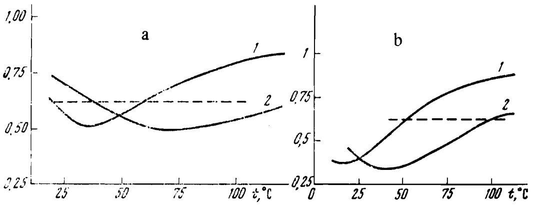

FIG. 10. Temperature dependence of $\alpha\Lambda/2\pi$ a) in salol, b) in benzophenone; 1—for frequency f = 0.9 GHz; 2—for f = 3 GHz.

the shift of the components of the wing fine structure in the high-temperature branch in all previous studies, actually define not V_T, but the quantity $(\eta/\rho\tau_1)^{1/2} \neq V_T$. For salol, it follows from (8) and the data of this paper that V_T changes at the frequency of the wing fine structure f = 0.54 GHz from 110 to 140 m/sec upon lowering of the temperature from 100 to 65°C, differing from the Newtonian value of the velocity V_N by 7% at t = 100°C and by 13% at t = 65°C. For benzophenone, V_T at the frequency of the wing fine structure f = 0.69 GHz changes from 120 to 180 m/sec in the temperature interval 112—44°C and differs from V_N at t = 112°C by 6% and at t = 44°C by 23%.

Detailed study of the wing fine structure of the Rayleigh line over a wide range of the viscosity of the medium has allowed us to make a significant step toward understanding of the nature of this phenomenon. In particular, it has been made clear in the optical studies that transverse sound waves that are more or less damped can propagate in low-viscosity liquids under certain conditions. A new direction is therefore set for acoustical investigations, and we think that the first step in this direction has been made in[36,37].

In conclusion, the authors express their thanks to V. P. Zaĭtsev for help in carrying out some of the experiments.

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1) The exciting light is propagated along the x axis, the scattered light is observed in the xy plane, the first index for I denotes the direction of polarization of the exciting light, and the second index the polarization of the scattered light (H is the horizontal polarization).

2) In the expression for I_{yH}, it has not been taken into account that the appearance of the maxima predicted by the Leontovich theory [27] is possible near the frequency of the Mandel'shtam-Brillouin components; these were apparently first observed by Stegeman and Stoicheff. [2]

3) In obtaining these relations in [17], it was assumed that R = const, but that T_τ can have any frequency dependence.

4) G. I. Kolesnikov took part in the measurements of D, τ_1 and τ_2 by the photoelectric method, and I. M. Grodnenskii participated in the measurements of $2\Delta\nu_m$, τ_1 and τ_2 by the photographic method in benzophenone.

5) A plot of $I\Delta\nu$ vs. $\Delta\nu$ was also constructed. On this plot, two maxima are easily distinguished, separated by the distances $\Delta\nu_1 \sim 1/\tau_1$ and $\Delta\nu_2 \sim 1/\tau_2$ from the frequency of the exciting light. A third straight-line portion was not observed on the dependence of $1/I$ on $(\Delta\nu)^2$, just as a third maximum was not discovered in the dependence of $I\Delta\nu$ on $\Delta\nu$. Therefore, we take two anistropy relaxation times into account. The same result was obtained for all the liquids previously studied. [28] This gave us a basis for considering only two relaxation times in the Rytov theory. [14,15]

6) If we take the model of diffusion rotary motion of the molecules, [27,30] which yields $\tau_1 = 4\pi r^3\eta/3kT$, where r is the radius of the molecule, we then obtain $r = 2.7 \times 10^{-8}$ for benzophenone and $r = 3.1 \times 10^{-8}$ cm for salol.

7) The authors are grateful to L. A. Zubkov for communicating his measured results for D of salol.

8) As has already been pointed out in [17], calculations of the shift of the wing fine structure components performed (see [8,15]) on the basis of analysis of the denominator only in Eq. (1) do not always give the correct result.

9) It is impossible to use here a stronger temperature dependence than $dV_T/dt = -3.6$ m/sec-deg, since we would have obtained a physically impossible result, namely: upon an increase in temperature, the quantity τ_M, after passing through a minimum, would begin to increase.

10) Calculation from Eq. (14) gives the temperature of the transition from one branch to the other as t = 1-10°C for benzophenone and t = 20°C for salol.

11) We note that in the low-temperature branch, one should not expect quantitative agreement of the conclusions of the Rytov theory, which is based on a relaxation scheme, with experiment. As has been shown earlier, [8,32-35] the relaxation theory does not describe the propagation of longitudinal and transverse sound in viscous media.

12) Here we are dealing with the minimum in the dependence of $\alpha\Lambda/2\pi$ (see Sec. 2) which arises in low-viscosity liquids in the presence of two relaxation times. Naturally, for high viscosities, in accord with theory, [17] $\alpha\Lambda/2\pi$ can become as small as we please.

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