Acoustic relaxation and the limb of the Rayleigh line in supercooled phenyl salicylate

L. M. Kashaeva, V. Yu. Lerman, R. L. Sabirov, T. M. Utarova, and Ya. T. Turakulov

Samarkand State University, Samarkand, Uzbekistan

The dynamics of the relaxation time of anisotropy fluctuations in supercooled phenyl salicylate has been studied on the basis of the spectra of anisotropic scattering of light. In addition, the velocity and absorption of sound in the ultrasonic and hypersonic frequency ranges have been studied. The observed velocity dispersion and the absorption of the sound are discussed on the basis of the theory of interacting modes. The relaxation time τ_{an} of the anisotropy fluctuations is related to the acoustic relaxation time τ over the entire temperature range studied by $\tau_{an} \approx 2\tau$, in agreement with the theoretical prediction.

For supercooled highly viscous liquids consisting of highly anisotropic molecules, such as phenyl salicylate and benzophenone, the viscosity of the liquid can vary by more than five orders of magnitude in a fairly narrow temperature interval (from -16 to $120\,°C$). Studies of hypersound propagation in phenyl salicylate (also known as salol) by various investigators[1-3] have demonstrated both a significant velocity dispersion and a maximum in the hypersound absorption at temperatures of order $50\,°C$. This absorption, as determined from the width of the Brillouin components, is much smaller than the so-called classical Stokes absorption, which is associated with the shear viscosity. Attempts to derive a quantitative description of sound propagation in viscous liquids on the basis of phenomenological theories have run into difficulties.[4-6] In the present paper we attempt to use the theory of interacting modes.

According to theoretical ideas based on the Ornstein–Zernike approximation, the dynamics of the interaction of longitudinal sound with anisotropy fluctuations in a liquid with anisotropic molecules capable of forming a mesophase results in dispersion and absorption of sound. It follows from the theory of Ref. 7 that the relation between the relaxation time τ_{an} of the anisotropy fluctuations found from the half-width of the limb of the Rayleigh line and the acoustic relaxation time τ is $\tau_{an} = 2\tau$. It was shown in Ref. 8 that this mechanism is described well in the isotropic phase of nematic liquid crystals by the equations of Ref. 7.

Phenyl salicylate, which is capable of undergoing supercooling, is also characterized by a substantial anisotropy of its molecules: The depolarization coefficient for scattered light in liquid phenyl salicylate is about 0.75. Over the temperature range from -16 to $120\,°C$, which includes the supercooled state, the relaxation time of anisotropy fluctuations, τ_{an}, varies by more than four orders of magnitude, in proportion to the change in the shear viscosity.

We have suggested that τ_{an} for supercooled phenyl salicylate is a temperature-dependent time scale which determines the interaction of anisotropy fluctuations with a corresponding acoustic mode.

In an effort to test this suggestion, we have studied the width of the Rayleigh line wing over a substantially expanded temperature range, and we have studied the char-

acteristics of sound propagation in phenyl salicylate over a substantially broader frequency range. Our intention here was to determine the temperature dependence of the kinetics of the anisotropy relaxation time and the acoustic relaxation time. For this study, we (first) used a spherical interferometer to study the depolarized scattering spectra. This approach allowed us to study anisotropy relaxation times on the order of 10^{-7} s. Second, we studied the characteristics of ultrasound propagation (at 5–25 MHz) for supercooled liquid phenyl salicylate (this was the first such study, to the best of our knowledge).

In this paper we analyze the experimental results on the propagation velocity and absorption of sound in phenyl salicylate on the basis of the theory of Ref. 7.

EXPERIMENTAL PROCEDURE

The temperature dependence of the velocity and absorption of ultrasound in phenyl salicylate was determined by measuring the diffraction of light by sound waves at frequencies of 5, 15, and 25 MHz using apparatus like that described in Ref. 9. The error of the velocity measurements was 0.5%, and that of the absorption measurements 10%.

In the hypersonic frequency range, the velocity and absorption of the sound were determined from the shift and width of Brillouin components in the spectra of scattered light found with spectral apparatus with a two-pass Fabry–Perot interferometer, as described in detail in Ref. 10. The sharpness of the interference pattern was on the order of 35, the contrast was $5 \cdot 10^4$, the scattering angle was 179°, and the wavelength was $\lambda = 632.8$ nm. The large scattering angle made it possible to significantly reduce the error in the determination of the hypersound propagation velocity, to less than 0.5%; the error in the absorption measurements was 10–15%, depending on the width of the Brillouin components. For the measurements at a large scattering angle we used the following self-collimation arrangement (Fig. 1): The velocity and absorption of the hypersound were measured over the temperature range from -40 to $+60\,°C$. The temperature was regulated with a TK-1 automatic thermoelectric chamber, which operates on the basis of the Peltier effect. The error of the temperature regulation was $\pm 0.5°$.
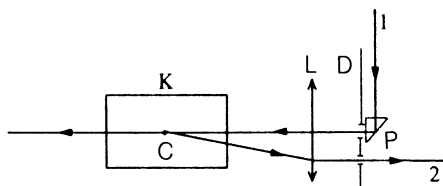
1063-7761/94/020195-05$10.00

FIG. 1. Self-collimation design for recording the spectra of scattered light of an angle of 179°. K—Cell; C—center of caustic; L—lens; D—diaphragm; P—rotatable prism; 1—laser beam; 2—light scattered at an angle of 179°.

Spectra of the depolarized scattering of light were measured on an apparatus with a spherical Fabry–Perot interferometer.[11] The dispersion region of the interferometer was $0.0166 \ cm^{-1}$, and the half-width of the instrumental function was $2 \cdot 10^{-4} \ cm^{-1}$. As the light source for exciting the scattering we used the beam from a single-frequency, frequency-stabilized He–Ne laser. The error in the measurements of the width of the Rayleigh line wing was 10%; it increased to 20% at low temperatures. To determine the actual half-width of the Rayleigh line wing we used the method developed in Ref. 12.

We processed the spectral widths δv to calculate the anisotropy relaxation times $\tau_{an} = 1/2\pi c \delta v$. The use of a spherical interferometer made it possible to study the temperature dependence of τ_{an} for values of δv inaccessible to study using a plane interferometer and a correlator.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the ultrasound velocity V for frequencies of 5, 15, and 25 MHz and of the hypersound velocity at frequencies of 7–11 GHz
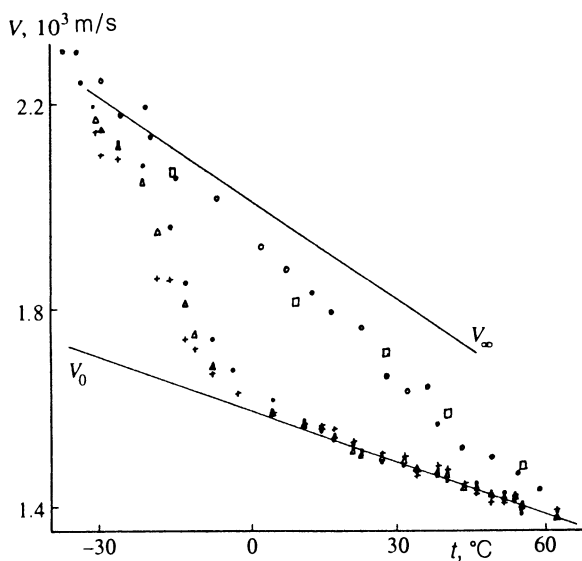

FIG. 2. Temperature dependence of the sound propagation velocity in phenyl salicylate at several frequencies. +—5 MHz; △—15 MHz; ●—25 MHz; ○—7–11 GHz (data of present study); □—6–10 GHz (Ref. 3).
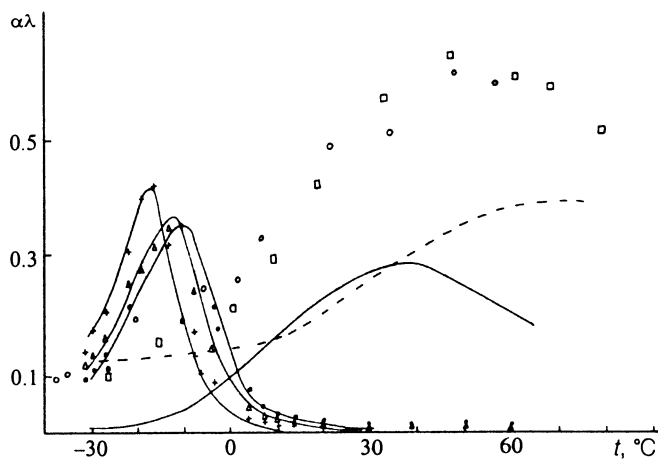

FIG. 3. Temperature dependence of the sound absorption multiplied by the wavelength at various frequencies. +—5 MHz; △—15 MHz; ●—25 MHz; ○—7–11 GHz (data of present study); □—6–10 GHz (Ref. 3). Solid lines) Theoretical; dashed line) difference between the experimental and theoretical values of $\alpha\lambda$ in the hypersonic region.

over the temperature range from −40 to 60 °C. Also shown here are values of the hypersound velocity from Refs. 1 and 3.

The values we found for the absorption coefficient α for ultrasonic and hypersonic frequencies are shown as a function of the temperature in Fig. 3. Also shown here are data on hypersound absorption from Ref. 3. As in the hypersonic frequency range, there is a maximum in the sound absorption at all the ultrasonic frequencies studied. It can be seen from Fig. 3 that the maximum of the ultrasonic absorption at 5 MHz occurs near a temperature of −17 °C, while the maximum at a frequency of 15 MHz is at a slightly higher temperature. We were unable to measure the upper part of the maximum at the frequency of 25 MHz, since the absorption was considerably above 20 cm^{-1} here. With these absorption coefficients, nonlinear effects of the ultrasonic pulses arise and lead to self-focusing of the ultrasound, as was shown in Ref. 13.

Figure 4 shows the relaxation time of the anisotropy fluctuations, τ_{an}, which we determined from the spectral width of the Rayleigh line wing in phenyl salicylate, along with some values from Ref. 14. Over the temperature range from −16 to 70 °C, τ_{an} varies by four orders of magnitude, in proportion to the change in the shear viscosity.[14,15]

We believe that the microscopic irregularities involved in the interaction which gives rise to features in the absorption and dispersion of the longitudinal sound velocity in highly viscous supercooled liquids are merely fluctuations of the short-range order or, equivalently, fluctuations of the anisotropy. Accordingly, τ_{an} should be equal to that temperature-dependent time scale which determines the interaction of the anisotropy fluctuations with the sound at various frequencies. In the isotropic phase of nematic liquid crystals, in which the anisotropy fluctuations are highly developed, as was shown in Ref. 9, a similar picture is observed. The only difference is that in the isotropic
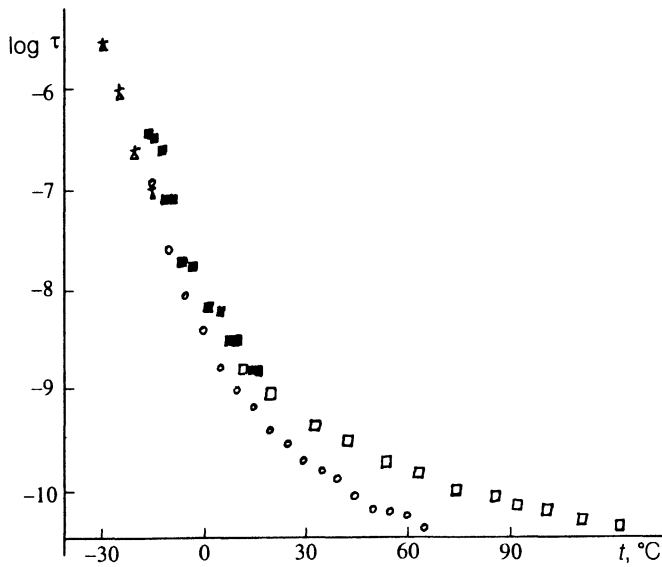
FIG. 4. Temperature dependence of the relaxation time of the anisotropy fluctuations, τ_{an}, and of the acoustic relaxation time τ. τ_{an}: Filled squares—data of present study; open squares—data of Ref. 14. τ: $+$) 5 MHz; $\triangle$) 15 MHz; $\bigcirc$) 7–11 GHz.

phase of a nematic liquid crystal the increase in τ_{an} toward the phase transition is due primarily to an increase in the susceptibility (the viscosity changes only very slightly), while in supercooled liquids the susceptibility remains essentially constant, as was shown in our own experiments and in Ref. 3, whereas the viscosity varies by four orders of magnitude. The latter variation is responsible for the corresponding increase in τ_{an}.

It was shown in Ref. 8 that in the isotropic phase of a nematic liquid crystal the dynamics of the interaction between longitudinal sound and the fluctuations of the anisotropy is described well by the equations of Ref. 7, which is based on the Ornstein–Zernike approximation. The theory predicts the following expressions for the dispersion of the sound velocity and for the excess absorption α, multiplied by the sound wavelength:

$$(V_\infty^2 - V_\omega^2)/V_\infty^2 = B(T)f_1(\omega\tau),\tag{1}$$

$$(\alpha\lambda)' = \pi B(T)f_2(\omega\tau).\tag{2}$$

Here $(\alpha\lambda)'$ is the excess sound absorption associated with the interaction of the longitudinal sound with the anisotropy fluctuations, V_ω is the sound velocity at the frequency ω, and V_∞ is the adiabatic velocity of longitudinal sound at frequencies at which the fluctuations are "frozen." The functions $B(T)$ are uniform functions for the velocity dispersion and the absorption, determined by the fluctuating part of the specific heat:

$$B(T) = \Delta C_p^{exc}/C_p^0,\tag{3}$$

$$f_1(\omega\tau) = \left(\frac{2}{\omega\tau}\right)^{1/2}\left[\frac{1}{\omega\tau}+\left(1+\frac{1}{\omega^2\tau^2}\right)^{1/2}\right]^{-1/2},\tag{4}$$

$$f_2(\omega\tau) = \left(\frac{2}{\omega\tau}\right)^{1/2}\left[\frac{1}{\omega\tau}+\left(1+\frac{1}{\omega^2\tau^2}\right)^{1/2}\right]^{-1/2} - \frac{2}{\omega\tau},\tag{5}$$

where τ is the acoustic relaxation time, and

$$\tau_{an} = 2\tau.\tag{6}$$

In the limit $\omega \to \infty$, the function f_1 approaches zero, while in the limit $\omega\tau \to 0$ we find $f_1 \to 1$. Accordingly,

TABLE I.

t, °C	V_0, m/s	V_∞, m/s	$B(T)_{disp}$	$B(T)_{sp\text{-}h}$
65	1370	1565	0.234	—
60	1390	1590	0.236	—
55	1405	1625	0.252	—
50	1420	1660	0.268	0.24
45	1440	1695	0.270	—
40	1455	1730	0.293	0.27
35	1470	1765	0.306	—
30	1490	1800	0.315	0.28
25	1505	1840	0.381	—
20	1525	1870	0.335	0.30
15	1540	1910	0.350	—
10	1558	1940	0.353	0.32
5	1575	1965	0.358	—
0	1593	2005	0.367	0.34
−5	1610	2045	0.380	—
−10	1627	2075	0.384	0.38
−15	1635	2110	0.392	—
−20	1651	2145	0.401	0.40
−25	1680	2180	0.406	—
−30	1698	2214	0.408	0.42

TABLE II.

t, °C	f = 5 μHz		f = 15 μHz		f = 25 μHz		f = 7–12 GHz	
	$\omega\tau$	$\tau \cdot 10^9$, s	$\omega\tau$	$\tau \cdot 10^9$, s	$\omega\tau$	$\tau \cdot 10^9$, s	$\omega\tau$	$\tau \cdot 10^9$, s
65	—	—	—	—	—	—	1.45	0.04
60	—	—	—	—	—	—	2.2	0.055
55	—	—	—	—	—	—	2.3	0.06
50	—	—	—	—	—	—	2.9	0.065
45	—	—	—	—	—	—	3.2	0.085
40	—	—	—	—	—	—	4.4	0.13
35	—	—	—	—	—	—	6.9	0.16
30	—	—	—	—	—	—	10.0	0.20
25	—	—	—	—	—	—	13.5	0.30
20	—	—	—	—	—	—	18.2	0.40
15	—	—	—	—	—	—	35.5	0.65
10	—	—	—	—	—	—	49.0	1.00
5	—	—	—	—	—	—	100	1.75
0	—	—	—	—	0.7	4.5	245	4.00
−5	—	—	0.8	8.5	1.4	8.8	556	9.00
−10	0.79	25	2.3	25	3.8	24	1585	25
−15	3.2	102	7.1	90	15.8	10	7000	110
−20	7.2	230	20	210	36	230	—	—
−25	27.5	880	65	850	115	850	—	—
−30	87	2800	200	2500	350	2500	—	—

knowing V_∞ and V_0, i.e., the velocities as $\omega\tau \to \infty$ and $\omega \to 0$, for the given relaxation process, we can determine $B(T)$ from Eq. (2):

$$B(T) = \frac{(V_\infty^2 - V_0^2)}{V_\infty^2 f_1(\omega\tau)}. \tag{7}$$

Using (1)–(7), we analyzed the experimental results for phenyl salicylate. From the experimental longitudinal sound velocities (Fig. 2) we determined V_∞ and V_0, and we calculated the function $B(T)$. The results of the calculation of $B(T)$ from the dispersion of the sound velocity are shown in Table I. Also shown here are values of $B(T)$ calculated from measurements of the specific heat[15] with the help of Eq. (3). It can be seen from Table I that there is a good agreement between the values of $B(T)$ calculated from the acoustic data and those found from the measured specific heat in phenyl salicylate. Knowing $B(T)$ and the values of $(V_\infty^2 - V_\omega^2)/V_\infty^2$, we can determine the function $f_1(\omega\tau)$ from Eq. (1) for the given frequency and temperature for each of the frequencies studied. From the value of $f_1(\omega\tau)$ found in this manner and Eq. (4), we find the value of $\omega\tau$ for each frequency and temperature studied. We thus find the value of τ for each temperature studied. Table II shows the results calculated for $\omega\tau$ and τ for each frequency studied and for each temperature.

Figure 4 shows values of τ from Table II calculated from the dispersion of the sound velocity. We see from this figure that τ and τ_{an} have the same temperature dependence, with a proportionality factor of order 2, in agreement with Eq. (6) of the theory of Ref. 7. This result is the first piece of support for our suggestion that the dynamics

of the anisotropy fluctuations determines the features observed in the propagation of sound in phenyl salicylate. The next step is to test the uniformity of the function $B(T)$ for the velocity dispersion and absorption of the sound. For this purpose, we use the values of $B(T)$ and $\omega\tau$ found from the dispersion of the sound velocity in phenyl salicylate to calculate $(\alpha\lambda)'$. This calculation was carried out as follows: Using $\omega\tau$, we calculated the function $f_2(\omega\tau)$ for each frequency and temperature. We then used this value to calculate $(\alpha\lambda)'$ from Eq. (2).

The solid lines in Fig. 3 show results calculated for $(\alpha\lambda)'$ for all the frequencies used. It can be seen from this figure that at ultrasonic frequencies there is a good agreement between the theoretical and experimental values of $\alpha\lambda$. At these frequencies, the contribution from other processes which dissipate the sound energy is negligible. It can thus be regarded as an established fact that the function $B(T)$ in Eqs. (1) and (2) for the dispersion and absorption of sound is uniform in the case of phenyl salicylate also. This result in turn confirms the existence of a single relaxation time, which corresponds to the relaxation time

TABLE III.

t, °C	$\tau \cdot 10^9$, s	f_r, GHz
60	0.08	2.0
30	0.12	1.4
−30	0.32	0.5

of anisotropy fluctuations in the phenyl salicylate.

Although the equations of the theory of interacting modes give a self-consistent description of the temperature dependence of the acoustic relaxation and the relaxation of the anisotropy over the entire temperature range studied, the values found theoretically for $(\alpha\lambda)'$ at hypersonic frequencies are considerably lower than the values found experimentally for $\alpha\lambda$. The difference between the experimental values of $\alpha\lambda$ and the theoretical values of $(\alpha\lambda)'$ is shown by the dashed line in Fig. 3. The shape of this line is characteristic of a relaxation process. Analysis of this process incorporating the regular part of the absorption at ultrasonic frequencies over the temperature range from 10 to 70 °C yields an estimate of the corresponding relaxation time at various temperatures.

For this estimate we used an expression describing the absorption of sound due to a single relaxation process in accordance with the Mandel'shtam–Leontovich relaxation theory:[16]

$$\frac{\alpha}{f^2} = \frac{A}{1 + (\omega\tau)^2} + C.$$

The value found for A from the regular part at ultrasonic frequencies over the temperature range from 10 °C to 70 °C was found to be constant at about $400 \cdot 10^{-17}\,\mathrm{cm}^{-1} \cdot \mathrm{s}^2$. We estimated the value of C from the regular part of the absorption at hypersonic frequencies, assuming that it depends only weakly on the temperature: $C \approx 4 \cdot 10^{-17}$ $\mathrm{cm}^{-1} \cdot \mathrm{s}^2$.

Estimates of the relaxation time of the second relaxation process are given in Table III, from which we see that the temperature dependence of the relaxation time for the second process is considerably weaker than that for the first process, associated with orientational motions of the molecules.

Since a limb with the corresponding half-width is not seen in the depolarized light scattering, we suggest that this relaxation process stems from translational modes of motion. Note that a relaxation process with similar relaxation times is observed in many liquids (benzene, toluene, the isotropic phase of liquid crystals, many aromatic compounds, etc.); further research is required to pin down its nature.

Since the relaxation frequency of this process is much higher than our ultrasonic frequencies, it is not manifested in the results of ultrasonic measurements. Here good agreement is observed between the experimental values of $\alpha\lambda$ and the values of $(\alpha\lambda)'$ calculated from Eq. (1).

[1] L. M. Sabirov, V. S. Starunov, and I. L. Fabelinski, Zh. Eksp. Teor. Fiz. **60**, 146 (1971) [Sov. Phys. JETP **33**, 82 (1971)].

[2] G. I. Kolesnikov, Trudy FIAN SSSR **118**, 58 (1980).

[3] C. H. Wang and J. Zhang, J. Chem. Phys. **85**, 794 (1986).

[4] S. V. Krivokhikha, Trudy FIAN SSSR **72**, 3 (1974).

[5] M. A. Isakovich and I. A. Chaban, Zh. Eksp. Teor. Fiz. **50**, 1343 (1966) [Sov. Phys. JETP **23**, 893 (1966)].

[6] I. A. Chaban, Zh. Eksp. Teor. Fiz. **85**, 186 (1983) [Sov. Phys. JETP **58**, 108 (1983)].

[7] H. Imura and K. Okano, Chem. Phys. Lett. **19**, 387 (1973).

[8] M. A. Anisimov, Critical Phenomena in Liquids and Liquid Crystals, Nauka, Moscow, 1987.

[9] V. Yu. Lerman, L. M. Sabirov, and T. M. Utarova, Zh. Eksp. Teor. Fiz. **103**, 2263 (1993).

[10] V. Yu. Lerman and L. M. Sabirov, Physics of the Liquid State, Kiev, 1986, Vol. 14, p. 22.

[11] V. Yu. Lerman, L. M. Sabirov, and T. M. Utarova, Zh. Eksp. Teor. Fiz. **96**, 2038 (1989) [Sov. Phys. JETP **69**, 1151 (1989)].

[12] H. C. Van de Hulst and J. J. M. Reesinck, Astrophys. J. **106**, 121 (1947).

[13] O. V. Belen'kaya, Ya. M. Zhileĭkin, G. A. Lyakhov et al., Akust. Zh. **38**, 984 (1992) [Sov. Phys. Acoust. **38**, 539 (1992)].

[14] G. D. Enright and B. P. Stoicheff, J. Chem. Phys. **64**, 3658 (1976).

[15] W. T. Laughlin and D. R. Uhlmann, J. Phys. Chem. **76**, 2317 (1972).

[16] L. I. Mandel'shtam and M. A. Leontovich, Zh. Eksp. Teor. Fiz. **7**, 437 (1937).

Translated by D. Parsons