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Spectra of molecular light scattering and some of their applications

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Contents

Abstract. Certain problems in the theory of the spectra of light scattered by optical inhomogeneities induced by fluctuations of different origin are discussed. Examples are given of the applications of light-scattering spectroscopy to the study of the propagation of hypersound in various substances and under different conditions, including the region of critical phenomena at phase transitions, the magnon spectra of ferromagnetic and antiferromagnetic materials, the Mandelstam – Brillouin spectra of piezoelectric semiconductors in static electric fields, the phonon bottleneck, the temperature dependence of the concentration-fluctuation correlation radius, the Mandelstam – Brillouin spectra in the presence of a steady-state temperature gradient, the fine structure of the Rayleigh line wing, and the propagation of transverse hypersound when the shear viscosity of a medium is varied over a wide range.

1. Introduction

Molecular light-scattering spectra carry extensive and varied information about the finest details of phenomena observed in the interaction of radiation with matter. Here, molecular light-scattering spectra are understood to be the changes in the frequency spectrum of exciting light or light incident on matter, which are induced by variation with time of fluctuations of different physical nature and which represent optical inhomogeneities leading to light scattering.

Molecular light scattering is defined as the scattering caused by optical inhomogeneities of fluctuation origin. Naturally, this is a fairly arbitrary definition, but this is the name by which this type of scattering has come to be distinguished from the combinational scattering of light (Raman effect) or from the light scattering by water droplets in a mist and in clouds and also by colloidal particles.

The development of the theory of molecular light scattering has proved to be so closely related to the theory of the specific heat of solids that without much error one could assume that both phenomena have a common origin.

Since the history of the theory of the specific heat is of interest, I shall now briefly recount the principal stages in the studies which have been carried out.

As early as the beginning of the previous century, P Dulong and A Petit (1819) established an empirical law that under normal conditions the specific heat of any solid is $C = 6\,\mathrm{cal\,mol^{-1}\,K^{-1}}$, explained on the hypothesis of a uniform distribution of energy among the degrees of freedom. However, a discrepancy between the predictions of the above law and the experimental results for certain substances, especially at low temperatures, required an improvement of the theory.

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In 1907, in his theory of the specific heat of a solid, Einstein [1] replaced the uniform distribution of energy among the degrees of freedom by the Planck distribution of energy between the frequencies of elastic vibrations. Einstein took here a qualitatively new step by applying Planck's law, previously used solely in emission theory problems, to the theory of elastic vibrations. However, Einstein considered only the average effective frequency of the particles constituting the solid.

Einstein's formula for the specific heat of a solid describes experimental results much more satisfactorily, although at very low temperatures the theory still needs improvement.

Einstein [1] did not discuss the problems of light scattering or of the diffraction of light by the elastic vibrations of a solid.

A striking phenomenon, involving a marked increase in the light scattering in a narrow temperature and pressure range at a phase transition and called the critical opalescence, has long been known and was finally explained correctly in 1908 by Smoluchovsky [2] as the result of a strong increase in the density fluctuations in pure liquids and in the concentration fluctuations in solutions.

In 1910 Einstein [3] employed Smoluchovsky's fruitful idea of fluctuations in a quantitative calculation of the intensities of light in liquids and solutions. In this calculation, Einstein expanded the density fluctuations as a three-dimensional Fourier series. The determination of the amplitudes of these series makes it possible to calculate the scattered-light intensity. Einstein not only obtained his famous formula for the scattered-light intensity but also devised the modern method for the calculation of fluctuations of any thermodynamic quantity using thermodynamic relations together with Boltzmann's statistical principle relating entropy to the probability of a closed system state. In his lengthy paper, Einstein says nothing about the specific heat of a solid. The component of the Fourier series are referred to as static 'waves'. In 1913 Mandelstam [4] superimposed surface fluctuation irregularities onto planar 'diffraction gratings'; in this case the surface 'grating waves' are static.

The next significant step was taken in 1912 by Debye [5], who tackled the still unsolved problem of the specific heat of a solid, especially at low temperatures, and developed in essence Einstein's theory already mentioned above.

In Debye's theory, a solid is regarded as a continuous medium but with a finite number of normal vibrations equal to $3N$ (where N is the number of atoms or molecules in a sample) and with the minimal wavelength of the elastic waves, which is determined by the interparticle distances, while the maximum frequency is correspondingly equal to the velocity of sound divided by the interparticle distance.

Debye says nothing about the scattering or diffraction of light by these dynamic elastic waves.

It was not until later that it became clear the Einstein's and Debye's studies of the theory of the specific heat of a solid, and Einstein's and Mandelstam's studies of the theory of molecular light scattering deal with waves of the same nature. One can even say that the Einstein and Mandelstam Fourier components and the Debye thermal elastic waves are the same thing.

However, it was not easy to understand this at the time the theory was proposed [6, Vol. 5], but the realisation of this identity has stimulated the development of optics and of molecular acoustics, and has led to the discovery of new phenomena and the appearance of new fields of experimental and theoretical research [7–10].

I shall return to this fundamental fact, but here I must make some comments on the calculation of fluctuations of thermodynamic quantities and of the intensity of light scattered by these fluctuations.

In a continuous medium ($\bar{l} \ll \lambda, \bar{l}$ is the mean free path and λ the wavelength of light), optical inhomogeneities arise as a consequence of the statistical nature of the motion of the particles constituting the medium.

Different quantities characterising the states of the substance may fluctuate. Only the fluctuations of physical quantities which lead to the appearance of an optical inhomogeneity in the investigated medium are significant for light scattering. These include the density and temperature fluctuations, and — in their turn — the density fluctuations depend on the pressure and entropy fluctuations.

Pressure fluctuations arise when particles with momenta somewhat smaller or greater than the volume-average momentum accumulate in a definite place and at a definite time while a fluctuation of temperature (ΔT) or entropy (ΔS) means that particles with a kinetic energy greater or smaller than the value averaged over the sample have gathered in a certain small region at a particular time.

Pressure fluctuations (ΔP) are quite independent of temperature fluctuations (ΔT) or entropy fluctuations (ΔS). This means that the statistical average products of the pressure and entropy fluctuations are zero.

Considering the entire picture, we can assume that the scattering as a consequence of pressure fluctuations at a particular point in a sample and at a particular time is unrelated to the same fluctuations at another point in the sample at the same time. This also applies to entropy fluctuations. Consequently, in order to calculate the intensity of light scattered as a consequence of fluctuations of different origin, it is sufficient to calculate the scattering by one fluctuation and to multiply the result by the number of such fluctuations in the scattering volume.

Calculations of the magnitude of the pressure, entropy, and concentration fluctuations by Einstein's method [3, 11–13] yield, for example, the following values for the pressure P, entropy S, and concentration C fluctuations:

$$\begin{aligned} \langle \Delta P^2 \rangle &= \frac{kT}{V^* \beta_S} , \\ \langle \Delta S^2 \rangle &= \frac{k C_P \rho}{V^*} , \\ \langle \Delta C^2 \rangle &= \frac{CkT}{V^* \partial P_1 / \partial C} . \end{aligned} \tag{1}$$

Here, V^*, β_S, P_1, C, T, and k are, respectively, the effective volume of the fluctuations, the adiabatic compressibility, the osmotic pressure, the concentration, the absolute temperature, and the Boltzmann constant. The angular brackets denote averaging over the ensemble.

Let us consider the case in which the effective dimensions of a fluctuation are much smaller than the wavelength λ of the scattered light. One can make the approximate assumption that $(V^*)^{1/3} = l_{\text{eff}} < \lambda/25$.

The intensity of the molecular light scattering due to fluctuations (1) is given by the following expression [11] for natural exciting light:

$$I_{\mathrm{ad}} = \frac{I_0 \pi^2 V}{2\lambda^4 L^2} \left(\rho \frac{\partial \varepsilon}{\partial \rho}\right)_S^2 \beta_S kT (1 + \cos^2\theta) \ , \tag{2}$$

where I_0 is the exciting-light intensity and L, ρ, and θ are, respectively, the distance between the scattering volume and the point of observation, the density, and the scattering angle;

$$I_{\mathrm{is}} = \frac{I_0 \pi^2 V}{2\lambda^4 L^2} \left(\frac{1}{\sigma} \frac{\partial \varepsilon}{\partial T}\right)_P^2 \frac{\sigma^2 kT^2}{C_P \rho} (1 + \cos^2\theta) \ , \tag{3}$$

where σ and C_P are, respectively, the coefficient of volume expansion and the heat capacity at constant pressure;

$$I_{\mathrm{c}} = \frac{I_0 \pi^2 V}{2\lambda^4 L^2} \left(\frac{\partial \varepsilon}{\partial C}\right)_{P,S}^2 \frac{CkT}{\partial P_1/\partial C} (1 + \cos^2\theta) \ , \tag{4}$$

where C is the concentration and P_1 the osmotic pressure.

The overall intensity of the light scattered by the density fluctuations in a liquid is [11]

$$I = I_{\mathrm{ad}} + I_{\mathrm{is}} = \frac{I_0 \pi^2 V}{2\lambda^4 L^2} \left[\left(\rho \frac{\partial \varepsilon}{\partial \rho}\right)_S^2 \beta_S kT + \left(\frac{1}{\sigma} \frac{\partial \varepsilon}{\partial T}\right)_P^2 \frac{\sigma^2 kT^2}{C_P \rho}\right] \times (1 + \cos^2\theta) \ . \tag{5}$$

If one assumes that

$$\left(\rho \frac{\partial \varepsilon}{\partial \rho}\right)_S^2 = \left(\frac{1}{\sigma} \frac{\partial \varepsilon}{\partial T}\right)_P^2 = \left(\rho \frac{\partial \varepsilon}{\partial \rho}\right)_T^2$$

and takes account of the familiar thermodynamic relationships [12]

$$\beta_T = \beta_S + \frac{\sigma^2 T}{\rho C_P} \tag{6}$$

(the subscript S denotes throughout the adiabatic value of a quantity and the subscript T corresponds to isothermal values), then the familiar Einstein formula is obtained instead of Eqn (5) [3, 9, 11, 12, 15]:

$$I = \frac{I_0 \pi^2 V}{2\lambda^4 L^2} \left(\rho \frac{\partial \varepsilon}{\partial \rho}\right)_T^2 \beta_T kT \ . \tag{7}$$

I emphasise that the light scattered as a consequence of the density fluctuations (I_{ad} and I_{is}) and the concentration fluctuations is in all cases linearly polarised for observations at the scattering angle $\theta = 90°$ relative to the electric field vector of the light wave (this vector is in a plane perpendicular to the scattering plane).

If the exciting light is linearly polarised in such a way that its electric field vector lies in the scattering plane, there is no scattered light (I and I_{c}) for observations at $\theta = 90°$. The light scattered by, for example, the anisotropy fluctuations is depolarised, but this is due to nonthermodynamic fluctuations which are discussed below.

In all these cases the optical inhomogeneities of fluctuation origin have been assumed to be static ('frozen') and independent of time, so that Eqns (2)–(5) and (7) yield the integral intensity.

Nevertheless, the fluctuations defined by Eqn (1) vary as a function of time, like statistical fluctuations in general, leading to fluctuations of the permittivity ($\Delta\varepsilon$) or of the refractive index (Δn) ($\varepsilon \equiv n^2$). They appear and are suppressed, appear again and are again suppressed, and so on. The mean square of a fluctuation $\langle \Delta\varepsilon^2 \rangle$ or its root-mean-square $\langle \Delta\varepsilon^2 \rangle^{1/2}$ is thus a function of time. The exciting light (with a certain frequency ω_0) incident on such a fluctuation is scattered sideways and the field of the scattered light wave is also a function of time. In other words, the time dependence of an optical inhomogeneity leads to modulation of the scattered light.

The modulation phenomenon occurs in a wide variety of fields in physics, radiophysics, and engineering. A theory of this phenomenon has been satisfactorily developed [6, 11, 15, 16]. In the case of light scattering, the modula-tion and the Doppler effect are the physical causes of a scattered-light spectrum differing from the exciting-light spectrum. Light scattering always occurs under the influence of exciting light and is therefore a stimulated process.

The theory of time dependence of the concentration fluctuations in a solution and of the density fluctuations in a liquid was developed in detail by Leontovich [7]. Its results have been applied to the problem of the scattered-light spectrum and a formula has been obtained for the frequency distribution of the scattered-light intensity. Our aim is in fact to do this for all possible fluctuations, but for the moment we shall deal with the pressure and entropy fluctuations or the temperature and concentration fluctuations.

Naturally, the time dependences of different fluctuations are different or, in other words, the modulation functions $\Phi(t)$ are different. We shall designate by $\Phi_P(t)$, $\Phi_S(t)$, $\Phi_C(t)$, etc. the root-mean-square values of the permittivity fluctuations determined by $\Delta P, \Delta S$, and ΔC. Suppose that the monochromatic light exciting the scattering is given by

$$E = E_0 \exp[\mathrm{i}(\omega_0 t - \boldsymbol{k}\cdot\boldsymbol{r})] \ .$$

The electric field of the scattered light can then be described by:

$$E'(t) = E(t)\Phi(t) \ . \tag{8}$$

It is necessary to find the law governing the variation of $\Phi(t)$ in order to obtain a specific form of $E'(t)$.

2. Mandelstam–Brillouin spectrum and Mandelstam–Brillouin scattering components

The function $\Phi(t)$ or the average fluctuation $\langle \Delta\varepsilon^2 \rangle^{1/2}$, induced by the pressure fluctuations, are described by the phenomenological equations which in fact apply to and have been formulated for the average values.

For the pressure fluctuations in an idealised medium, free of losses and dispersion, this is a wave equation of the type

$$\ddot{\Phi} - v^2 \nabla^2 \Phi = 0 \ . \tag{9}$$

Since any function of a known argument $t - (r/v)$ can be a solution of wave equation (9), we shall proceed in the usual way and seek its solution in the form

$$\Phi(t) = \Phi_0 \cos(\Omega_0 t - \boldsymbol{q}\cdot\boldsymbol{r} - \varphi) \ , \tag{10}$$

where $\Phi_0, \Omega_0, \boldsymbol{q}$, and $\boldsymbol{r}$ are, respectively, the maximum value of $\Phi(t)$, the angular frequency, the wave vector, and the coordinate respectively, while v is the velocity of sound.

Thus, in this case the modulating function $\Phi(t)$ varies in accordance with the cosine law and $E'(t)$ can be readily determined from Eqns (8) and (10):

$$E'(t) = \frac{\Phi_0 E_0}{2} \exp\left[\!\left[\mathrm{i}[(\omega_0 + \Omega_0)t - \boldsymbol{q}\cdot\boldsymbol{r} - \varphi]\right\} + \exp\left\{\mathrm{i}[(\omega_0 - \Omega_0)t + \boldsymbol{q}\cdot\boldsymbol{r} + \varphi]\right\}\right]\!\!\right] \ . \tag{11}$$

It follows from Eqn (11) that there are two satellites in the scattered-light spectrum: a Stokes satellite with a frequency $\omega_0 - \Omega_0$ and an anti-Stokes satellite with a frequency $\omega_0 + \Omega_0$; according to Eqns (9) and (10), the elastic wave frequency is $\Omega_0 = vq$.

The satellites arising in the course of the modulation of the scattered light are known in Western literature as the Brillouin components, but they were first predicted independently by Mandelstam [17] and Brillouin [18]. Mandelstam also carried out an experimental search for the phenomenon which he predicted. On Landsberg's and Mandelstam's suggestion, Gross [19] joined this investigation and detected the Mandelstam–Brillouin (MB) components in a quartz single crystal with the aid of improved apparatus. Gross also observed the same phenomenon in liquids.

It follows from the law of conservation of energy and momentum that

$$\omega_0 - \omega_s = \pm\Omega_0, \quad \boldsymbol{k}_0 - \boldsymbol{k}_s = \pm\boldsymbol{q} \ , \tag{12}$$

where ω_s is the scattered-light frequency, Ω_0 the frequency of the elastic (sound) wave, and $\boldsymbol{k}_s$ and $\boldsymbol{q}$ are the wave vectors of the scattered light and the elastic wave, respectively (Fig. 1).

Since Ω/ω_0 is small ($\sim 10^{-5}$), one can put $|\boldsymbol{k}_s| \approx |\boldsymbol{k}_0|$, while

$$|q| = \frac{2\pi}{\Lambda} = \frac{4\pi n}{\lambda} \sin\frac{\theta}{2} \ . \tag{13}$$

Here, Λ is the wavelength of the elastic waves and θ the scattering angle. The relationship between Ω_0, q, and v follows from Eqn (12):

$$\Omega_0 = vq = \frac{4\pi n v}{\lambda} \sin\frac{\theta}{2} = 2n\frac{v}{c}\omega_0 \sin\frac{\theta}{2} \ . \tag{14}$$

Hence, the shift of the frequency Ω relative to ω_0 is proportional to the ratio of the velocity of sound v to the velocity of light c, as well as to the refractive index and the sine of half the scattering angle:

$$\frac{\Delta\omega}{\omega_0} = \pm 2n\frac{v}{c}\sin\frac{\theta}{2} \ . \tag{15}$$

where $\Delta\omega$ is the frequency shift of a an MB component.

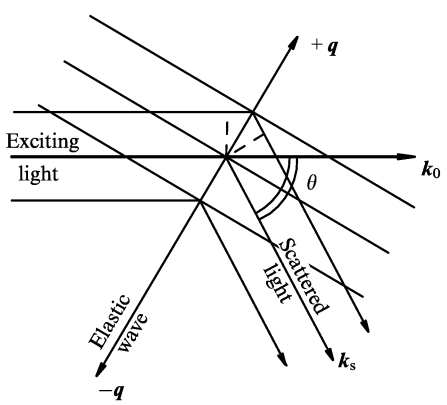

Figure 1. Scattering (diffraction) of light by an elastic acoustic wave representing the Fourier component of a pressure fluctuation. The wave vectors represent the exciting light ($\boldsymbol{k}_0$), the scattered light ($\boldsymbol{k}_s$), and the elastic wave ($\boldsymbol{q}$).

It follows from Eqns (14) and (15) that the investigated sound frequency Ω_0 can be varied between wide limits by varying the angle of observation of the scattered light from $\Omega_0 = 0$ for $\theta = 0$ to $\Omega_0 = 2n(v/c)\omega_0$ for $\theta = 180°$.

For $\omega_0 = 5 \times 10^{15}\,\mathrm{rad\,s^{-1}}$, we obtain $\Omega_0 \approx 5 \times 10^{10}\,\mathrm{rad\,s^{-1}}$ or $f \approx 10^{10}\,\mathrm{Hz}$ for water, where $v = 1.5 \times 10^5\,\mathrm{cm\,s^{-1}}$ and the green-light refractive index is $n = 1.33$. For diamond, Ω_0 is an order of magnitude higher than for water.

It is thus possible to investigate sound waves of frequencies which may be varied by several orders of magnitude by varying the scattering angle. Studies at hypersonic frequencies $\Omega_0 > 10^9 - 10^{10}\,\mathrm{Hz}$ are especially effective. The details will be given later.

Elastic or sound and hypersound waves are the Debye thermal waves and their number is $2N$, where N is the number of molecules or species within the volume of a sample. These extremely numerous sound waves propagate along very diverse directions within a bulk sample and, at first sight, it appears that there is no hope whatever of investigating the properties of matter at any one frequency Ω_0 with a wave vector $\boldsymbol{q}$. However, this would be a premature conclusion. Fig. 1 helps one to understand how this can be achieved experimentally. If a plane light wave with a wave vector $\boldsymbol{k}_0$ is incident on a sample and observations are made in the direction of the wave vector $\boldsymbol{k}_s$, then in the same direction $\boldsymbol{k}_s$ one can observe light diffracted by a grating formed by a standing wave with wave vectors $\pm\boldsymbol{q}$ which satisfy Eqn (12) or Bragg's condition. This condition can be formulated as follows:

$$2\Lambda n \sin\frac{\theta}{2} = \lambda \ , \tag{16}$$

where Λ is the period of this grating or the wavelength of the sound, and λ is the wavelength of light in vacuum.

One may speak of the formation of a standing grating because among the many sound waves there are always some having wave vectors identical in magnitude but with opposite directions [11].

An expression for the field of the scattered light [Eqn (11)] is obtained by taking account of the modulation of the scattered light.

Using Eqn (11), we obtain an expression for the time variation of the intensity:

$$E'(t)E'^*(t) = I(t) = I_0\left[1 + \cos(2\Omega_0 t - 2\boldsymbol{q}\cdot\boldsymbol{r})\right] \ . \tag{17}$$

Here

$$I_0 = \frac{(E'_0\Phi_0)^2}{2}$$

[see Eqns (10) and (11)]. Eqn (17) shows that the expression for the intensity of the MB components contains a time-independent constituent equal to I_0 and, against the background of a constant intensity, there is an intensity which varies at a frequency $2\Omega_0 \approx 2 \times 10^{10}\,\mathrm{Hz}$. At the maximum, the variable constituent is I_0, while at the minimum it is determined by the constant constituent also equal to I_0. Thus, the overall maximum intensity is $2I_0$.

Hence, in our idealised model, with no losses or dispersion of the velocity of sound in matter, the scattered-light spectrum of a liquid phase exhibits two MB scattering components arranged symmetrically relative to ω_0. In this model the MB components do not have a finite width; they are represented by a δ-function. For an isotropic body, such as a glass, one

observes two MB components due to longitudinal sound and two components due to transverse sound. In the case of an anisotropic crystal, the formula for the frequency of sound Ω_0 or for the optical shift in the spectrum $\Delta\omega$ is [26]

$$\Omega_0 = \omega_0 \frac{v(q)}{c} \sqrt{(n_\mathrm{i} - n_\mathrm{s})^2 + 4 n_\mathrm{i} n_s \sin^2 \frac{\theta}{2}} \ . \tag{18}$$

Here, n_i and n_s are the refractive indices for the incident (exciting) and scattered light respectively.

One quasilongitudinal and two quasitransverse waves ('fast' and 'slow') can propagate in any direction in a crystal and the positions of the MB components differ in the two polarisation states of the exciting light and in the two polarisations of the scattered light, so that the total number of components may be 24, but — for certain polarisations and orientations of the crystal — it is possible to observe six components of the spectrum simultaneously. Fig. 2 shows four MB scattering components.

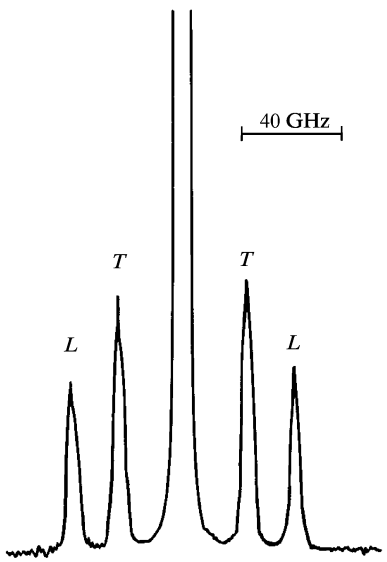

Figure 2. Spectrum of light scattered in yttrium aluminium garnet ($Y_3Al_5O_{12}$) [89]. Here, L and T are the MB scattering components due to longitudinal and transverse elastic waves, respectively.

More information can be deduced from the scattered light spectrum if the function $\Phi(t)$ is found for a more realistic medium in which there are losses but the dispersion is neglected.

It is then necessary to describe $\Phi(t)$ by the phenomenological hydrodynamic equation for the average values, i.e. the Stokes equation [7, 11, 23, 24]:

$$\ddot{\Phi} - v^2 \nabla^2 \Phi - \Gamma \nabla^2 \dot{\Phi} = 0 \ . \tag{19}$$

Here,

$$\Gamma = \frac{1}{\rho} \left[\frac{4}{3} \eta + \eta' + \frac{\kappa}{C_P} (\gamma - 1) \right] \ , \tag{20}$$

where η' is the bulk viscosity, κ the thermal conductivity, $\gamma = C_P / C_V$, and C_P and C_V are the specific heats at constant pressure and constant volume, respectively.

The solution of Eqn (19) will be sought in the form of an expansion representing a three-dimensional Fourier series of the type

$$\Phi(t, r) = \sum_q \Phi(t) \exp(\mathrm{i} \boldsymbol{q} \cdot \boldsymbol{r}) \ . \tag{21}$$

Substitution of Eqn (21) in Eqn (19) gives the following expression for one of the components of the sum (21):

$$\ddot{\Phi} + \Gamma q^2 \dot{\Phi} + v^2 q^2 \Phi = 0 \ . \tag{22}$$

The Laplace transform

$$\Phi(p) = \int_0^\infty \Phi(t) \exp(-pt) \, \mathrm{d}t \tag{23}$$

applied to Eqn (22) yields the following expression for $\Phi(p)$:

$$\Phi = \frac{\phi(t=0)[p + \Gamma q^2 + \dot{\Phi}(t=0)]}{p^2 + p q^2 \Gamma + v^2 q^2} = \frac{\Phi(0)[p + 2\delta + \dot{\Phi}(0)]}{p^2 + 2\delta p + \Omega_0^2}, \tag{24}$$

where

$$\delta = \frac{1}{2} \Gamma q^2 , \quad \Omega_0^2 = v^2 q^2 \ . \tag{25}$$

The time dependence in the modulating function $\Phi(t)$ is obtained from Eqn (24) by the inverse Fourier transformation:

$$\Phi(t) = \Phi(0) \exp(-\delta t) \left[\cos(\Omega_0^2 - \delta^2 t)^{1/2} + \sin(\Omega_0^2 - \delta^2 t)^{1/2} \right]. \tag{26}$$

When p is replaced by $\mathrm{i}\omega$ in the Laplace transform, the latter becomes a Fourier integral and then, if Eqn (23) is multiplied by $\Phi(0)$ and it is assumed that $\langle \Phi(0) \dot{\Phi}(0) \rangle = 0$, the result is the following expression for the intensity distribution [7]:

$$I(\omega) \sim E_0^2 \langle |\Phi(\omega)|^2 \rangle = E_0^2 \, \mathrm{Re} \int_0^\infty \Phi(0) \Phi(t) \exp(-\mathrm{i}\omega t) \, \mathrm{d}t$$

$$= E_0^2 \langle |\Phi(0)|^2 \rangle \frac{2\Omega_0^2 \delta}{(\omega^2 - \Omega_0^2)^2 + 4\delta^2 \omega^2} \ . \tag{27}$$

Integration of Eqn (27) over all the frequencies should give the intensity I_ad of the light scattered by the adiabatic density fluctuations [Eqn (2)]. Hence, the normalisation conditions yield

$$I_\mathrm{ad} = \int_{-\infty}^\infty I(\omega) \, \mathrm{d}\omega = E_0^2 \Phi^2(0) \int_{-\infty}^\infty \frac{2\Omega_0^2 \delta \, \mathrm{d}\omega}{(\omega^2 - \Omega_0^2)^2 + 4\delta^2 \omega^2}$$

$$= \pi E_0^2 \Phi^2(0) \ ; \tag{28}$$

it therefore follows that

$$I(\omega) = I_\mathrm{ad} \frac{(2/\pi) \delta \Omega_0^2}{(\omega^2 - \Omega_0^2)^2 + 4\delta^2 \omega^2} \ . \tag{29}$$

If

$$\delta \ll \Omega_0 \ , \tag{30}$$

then

$$I(\omega) = I_\mathrm{ad} \frac{\delta/\pi}{(\omega - \Omega_0)^2 + \delta^2} \ . \tag{31}$$

It follows from Eqn (31) that the overall width of a Brillouin scattering component at half the maximum intensity is

$$(\delta\omega)_\mathrm{B} = 2\delta \ . \tag{32a}$$

Eqn (29) was obtained in a different way by Ginzburg [8, 9]. The factor representing decay with time can be expressed

simply in terms of the amplitude absorption coefficient α, namely,

$$\delta = \alpha v \ , \tag{32b}$$

where v is the velocity of sound.

On the other hand, the hydrodynamic theory yields the following expression for α:

$$\alpha = \frac{q^2}{2v}\Gamma \ , \tag{33}$$

where Γ is defined by Eqn (20). Substitution of Eqn (33) in Eqn (32) gives

$$2\delta\omega_{\mathrm{B}} = q^2\Gamma. \tag{34}$$

Consequently, if the molecular scattering spectrum is suitably recorded, it is possible to find the phase velocity of sound from the positions of the MB components, while the sound or hypersound decay factor can be found from half the width of these components. Thus, a new field of optical and acoustic research has arisen. The dispersion of the velocity of sound [20, 21] has been observed by means of such procedures, and hypersound relaxation and absorption process in liquids have been investigated quantitatively [22]. Many phenomena also affect the intensity of MB components, but this will be discussed in detail below.

However, it must be emphasised that the elastic thermal or Debye waves differ significantly from the elastic acoustic waves, which are generated by an emitter and are then injected into the medium being investigated.

A plane radiation wave then generated is

$$A = A_0 \exp[\mathrm{i}(\Omega_{\mathrm{a}} t - Qx)] \ , \tag{35}$$

where A_0, Ω_{a}, and Q are the amplitude, the frequency, and the wave number of the sound wave, respectively.

If $A = A_0$ at time $t = 0$ and at a point in space $x = 0$, then this wave is described by Eqn (35) as time progresses and the wave propagates in the medium.

If the medium suffers acoustic losses under these conditions, the implication is that the frequencies Ω_{a} or Q are complex variables. For example, we may assume that

$$\Omega_{\mathrm{a}} = \Omega_1 + \mathrm{i}\Gamma \ . \tag{36}$$

Substitution of Eqn (36) in Eqn (35) yields

$$A = A_0 \exp(-\Gamma t) \exp[\mathrm{i}(\Omega_1 t - Qx)] \ . \tag{37}$$

It follows from the last expression that the amplitude of the sound wave may decay as a function of time and, when account is taken of Eqn (32), it can also be attenuated in space. It is easy to show that Γ represents the same quantity in Eqns (37) and (33) [14, 23–25].

In the case of the thermal elastic or Debye waves, the situation is completely different.

According to the Debye theory [5], an average energy $\hbar\Omega[\exp(\hbar\Omega/kT) - 1]^{-1}$ corresponds to each normal vibration and, bearing in mind that $\hbar\Omega/kT \ll 1$, an average energy kT corresponds to each normal vibration in the MB spectrum. Hence it follows that at a temperature T the elastic thermal or Debye waves retain a constant amplitude A and therefore this amplitude [Eqn (37)] does not decay in the usually accepted sense. At a constant temperature T, the amplitude of the thermal wave is constant at any point within a sample and at any time, and it can be described in terms of a combination of constants, the velocity of sound, and the frequency interval.†

The natural conclusion following from all the foregoing considerations is that, having the MB spectrum at one's disposal and knowing the intensity distribution in the MB components, it is possible to find the decay factor of the sound wave, generally speaking in the range from $\Omega = 0$ to $\Omega = 2n(v/c)\omega_0$. However, we emphasise once again that this possibility arises not because the thermal elastic wave decays, but because the modulating function for the time variation of $\Phi(t)$ includes as parameters quantities such as the viscosity, which determines the elastic perturbation losses, the frequency, and the elastic-vibration wave vector.

3. Some applications of Mandelstam–Brillouin spectroscopy

As already mentioned above, the first effective application of MB spectroscopy was made by me together with Shustin [20] and Molchanov [21] in connection with the observation of the dispersion of the velocity of sound in benzene, carbon tetrachloride, chloroform, carbon disulfide, and then also in a series of other liquids.‡ We measured the hypersound absorption coefficient α only after laser light sources became available in our laboratory [22]. We found that $\alpha = 4.5 \times 10^3\ \mathrm{cm}^{-1}$ for benzene and $\alpha = 1.6 \times 10^4\ \mathrm{cm}^{-1}$ for carbon tetrachloride.

The technique used by us in the measurement of the dispersion of the velocity of sound and of the absorption coefficient made it possible to carry out a direct experimental test of a formula from the relaxation theory, developed by Mandelstam and Leontovich [29], and to determine the relaxation time τ of the bulk viscosity. For example, $\tau = 2.7 \times 10^{-10}$ s for benzene and $\tau = 28.3 \times 10^{-10}$ s for carbon disulfide. The relaxation time τ has also been found for other liquids.

One can say that the experimental studies described here have laid the foundations of a new quantitative method for investigating the optical and acoustic properties of matter in a wide variety of states, for example in the course of phase transitions in the critical region, in paramagnetic materials under the phonon 'bottleneck' conditions, in magnetic materials, in piezoelectric semiconductors subjected to an external static electric field, in transparent and opaque insulators, in semiconductors and metals, and in viscous liquids and glasses. Naturally, this list does not exhaust the numerous applications of this method.

† In order to estimate the effective amplitude A_{eff} of a thermal wave, one may postulate that in the range $\mathrm{d}\Omega$ for $\hbar\Omega/kT \ll 1$ the wave energy can be determined from Planck's formula (Rayleigh–Jeans formula) $E_\Omega\,\mathrm{d}\Omega = (\rho\pi^2 V^3)^{-1}\Omega^2 kT\ \mathrm{d}\Omega$ or $\rho\Omega^2 A_{\mathrm{eff}}^2 = (\rho\pi^2 V^3)^{-1}\Omega^2 kT\ \mathrm{d}\Omega$, so that

$$A_{\mathrm{eff}} = \sqrt{\frac{kT}{\rho^2\pi^2 V^3}\,\mathrm{d}\Omega} \ .$$

It is natural to adopt the true half-width of the MB components as $\mathrm{d}\Omega$. For example, $\mathrm{d}\Omega \approx 10^9\ \mathrm{rad\,s^{-1}}$ for liquid benzene at $T = 300\,^\circ\mathrm{C}$ and an estimate yields $A_{\mathrm{eff}} = 3 \times 10^{-10}$ cm.

‡ It is noteworthy that an attempt to use the MB components for the determination of the velocity of hypersound had been undertaken much earlier [28], but it was unsuccessful: a positive dispersion of the velocity of sound, expected for a series of liquids, was not observed.

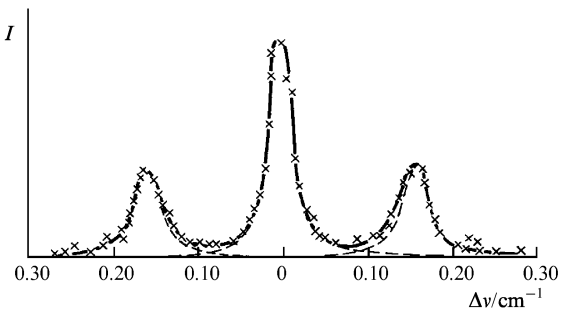

Figure 3. Spectrum of light scattered in liquid benzene [11, 22].

The first reported spectrum of the molecular scattering of He–Ne laser radiation in benzene [22] will be considered as an example. This spectrum can be used to determine the amplitude absorption coefficient α of hypersound and its velocity with the aid of Eqns (31) and (15) (Fig. 3).

The MB spectra also make it possible to investigate the propagation of hypersound in the region of the liquid–vapour phase transition as well as in liquid solutions. The temperature dependence of the velocity of sound near the phase transition in carbon dioxide (CO_2) was determined above and below the critical temperature from the positions of the MB components [44].

The propagation of hypersound in the region of the upper, lower, and double critical points in a guaiacol–glycerol solution with some added water has been recently investigated. In the presence of a small amount of water in this solution, a closed region or a loop appears in the phase diagram (representing the dependence of the temperature T on the concentration C), within which the solution components are immiscible whilst outside it the solution is homogeneous. Fig. 4 gives the dependence of the velocity of hypersound in the region of the upper and lower critical points of a solution of this kind in which the temperatures of the upper and lower points differ by only 7 K. The fact that near the lower critical point the temperature coefficient of the velocity of hypersound exceeds by a factor of 2 the coefficient in the region of the upper critical point is not trivial. It awaits explanation.

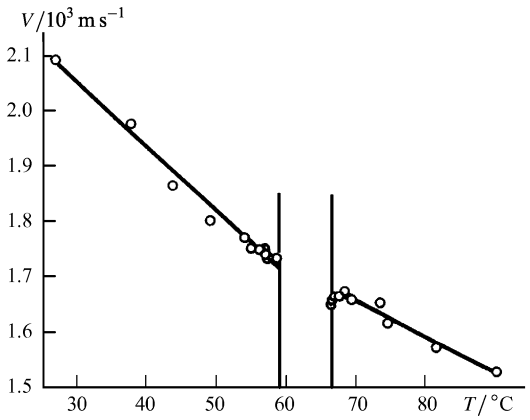

Figure 4. Temperature dependence of the velocity of hypersound near the upper and lower critical points of a guaiacol–glycerol solution [155].

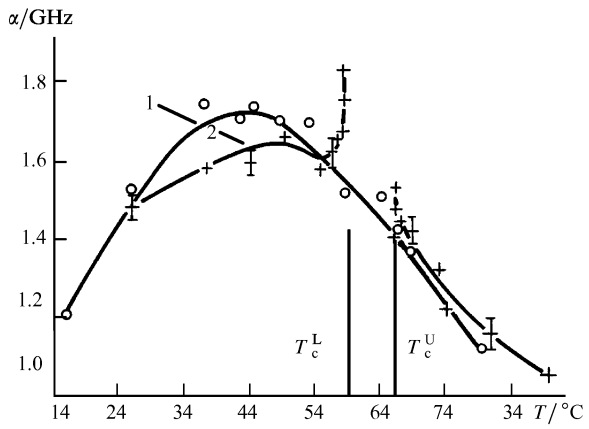

Figure 5. Temperature dependence of the absorption coefficient of hypersound near the upper and lower critical points of a guaiacol–glycerol solution [155].

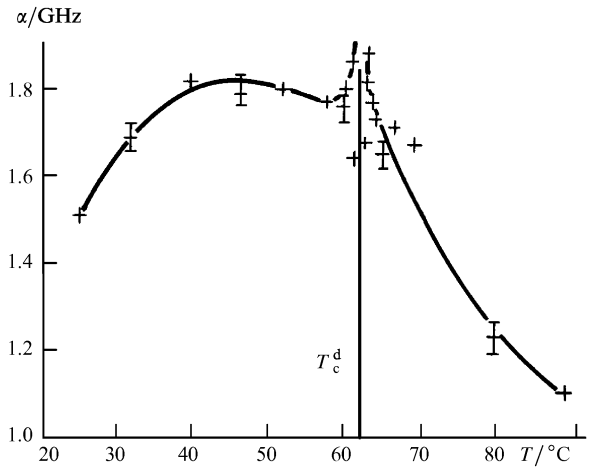

Figure 6. Temperature dependence of the absorption coefficient of hypersound near the double critical point of a guaiacol–glycerol solution [155].

Fig. 5 illustrates the absorption of hypersound, represented by the width of the MB component in the same solution in the region of the upper and lower critical points.

Fig. 6 shows the hypersound absorption curve in the region where the upper and lower points merge forming a double critical point.

The anisotropy of the elastic constants as well as their temperature dependences can be investigated in detail on the basis of measurements of the velocity of hypersound in crystals along different crystallographic directions. The behaviour of the elastic constants in the region of a phase transition is particularly interesting. A strong anomaly of the elastic constant $C_{66} = \rho v^2$ has been deduced from the positions of the MB components in a potassium dihydrogen phosphate (KDP) crystal in the region of the ferroelectric phase transition [30].

Very many publications, difficult to survey, have been devoted to the applications of molecular light-scattering spectroscopy to solids. These include the series of books entitled *Light Scattering in Solids* edited by M Cardona and G Guntherodt [31]. Here, solids are understood to comprise insulators, semiconductors, metals, superionic conductors, and glasses.

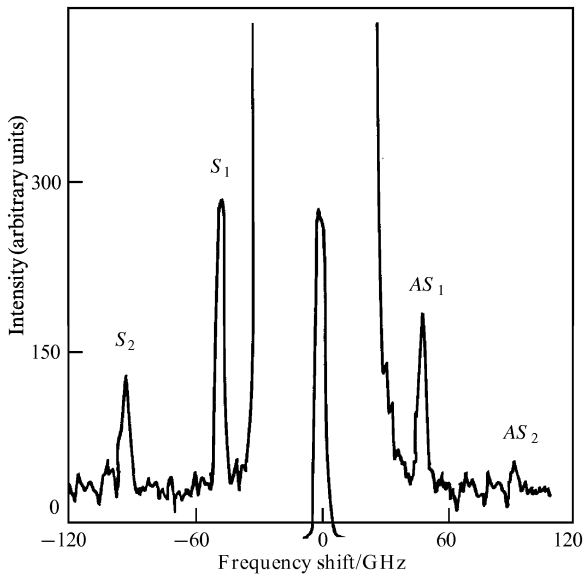

Figure 7. MB spectra of anitferromagnet EuTe: temperature 1.5 K, scatering angle $\theta = 180°$, $q = 3 \times 10^5\ \mathrm{cm}^{-1}$; $\boldsymbol{H}||[001]$, $H = 25$ kOe; MB scattering components S_1 and AS_1 correspond to the lf magnon branch, and S_2 and AS_2 to the hf magnon branch. The position of the MB components varies with the magnetic field [36b].

The spectra of MB scattering by spin waves in ferromagnetic and antiferromagnetic materials are of great interest. Following the first investigations by P A Fleury et al. [32, 33], extensive theoretical and experimental studies have been carried out and reviews and monographs have been written [34]. As an illustration, Fig. 7 presents the MB spectrum of EuTe [Refs 36a and 36b]. MB spectroscopy is also effective in the study of acoustic paramagnetic resonance (APR) [35]. The effect known as the phonon 'bottleneck' is particularly interesting and its basic nature can be explained as follows.

In a paramagnetic crystal, the levels of the incorporated ions (for example, Ni^{2+} or Ce^{33+}) are split in a static magnetic field and two levels with an energy difference ΔE are formed in the simplest case. If such a system is acted upon by a high-frequency electromagnetic field with $\hbar\omega = \Delta E$, the usual ESR line is observed. The absorbed energy is consumed in resonant 'excitation of spins'. If the spin excitation energy flux to the crystal lattice is greater than the energy flux from the crystal lattice to the thermostat (liquid helium), the number of phonons with an energy $\hbar\Omega \approx \hbar\omega$ exceeds the equilibrium value. Consequently, in the range of frequencies not exceeding the paramagnetic resonance line width, the nonequilibrium temperature T_{ne} exceeds the equilibrium temperature T_{e}. The quantity $\sigma = T_{\mathrm{ne}}/T_{\mathrm{e}}$, which may be calculated, is referred to as the phonon 'bottleneck' factor.

If the MB components are now observed in light scattered in a crystal exhibiting the phonon 'bottleneck' effect in such a way that the components are induced by the resonance phonons $\hbar\Omega$, the intensity of these components is greater than for a crystal at the temperature of the heat reservoir surrounding it. Such experiments have been carried out by Brya et al. [37] on an MgO crystal with Ni^{2+} ions and by Al'tshuler et al. [38] on double cerium nitrate with Ce^{3+} ions. In the case of MgO crystals, the temperature of the reservoir was 2 K and the intensity of the MB components corresponding to 60 K or $\sigma = 30$. In the study of double cerium nitrate, the temperature of the reservoir was 1.5 K and the intensity of the MB components corresponded to 100 K and hence to $\sigma = 70$. There are also data obtained by both groups which give σ exceeding 1000. This procedure for the study of APR can yield information about the most detailed aspects of the phenomenon.

A striking and impressive phenomenon is displayed in the spectrum of light scattered in piezoelectric semiconductors in a static electric field. Little more than 30 years ago it was established that, under certain conditions, an ultrasonic wave propagating in a piezoelectric semiconductor can actually be enhanced rather than, as usual, attenuated [39, 40]. These conditions include the application of an external static electric field of intensity E capable of accelerating charge carriers to velocities equal to or greater than the phase velocity of sound. ZnO and CdS are examples of such substances. Calculations have shown that the sound damping factor is

$$\Gamma = \Gamma_0 + \frac{\chi[1 - (E/E_{\mathrm{c}})]\omega\tau q}{(1 + q^2R^2)^2 + [1 - (E/E_{\mathrm{c}})]^2\Omega^2\tau^2}\ , \qquad (38)$$

where Γ_0 is the absorption by the crystal lattice; $\tau = \varepsilon/4\pi\sigma$; ε is the permittivity; σ is the conductivity; χ is the electromechanical coupling constant; Ω is the sound frequency; q is the wave number; R is the Debye radius.

If the second term of Eqn (38) becomes negative for $E/E_{\mathrm{c}} > 1$ and Γ is negative, which can be readily realised, the ultrasonic wave defined by Eqn (37) does not decay, but is actually amplified.

Naturally, the amplification takes place within a certain band of frequencies, and the gain maximum in this band corresponds to the frequency $\Omega_{\max} = v/R$. Here R is the Debye radius

$$R = \sqrt{\frac{\varepsilon kT}{4\pi n_0 e^2}}\ ,$$

and n_0 is the number of carriers of a charge e in $1\ \mathrm{cm}^3$.

If the frequency of the elastic thermal wave responsible for the appearance of a an MB component lies within the band of the amplified elastic wave frequencies of a semiconductor, the molecular light scattering spectrum should change. If the elastic wave which is amplified has the frequency, polarisation, and direction of propagation such that it generates a Stokes (or anti-Stokes) MB component, then this component should increase appreciably compared with the other component. This phenomenon was in fact first observed in Wetling's experiments [41] and was thoroughly investigated by Yakovlev and his colleagues (see Ref. [42] and the literature cited there).

Fig. 8 presents the spectrum of the MB components of light scattered in a ZnO single crystal subjected to a static electric field [43].

Experiments have shown that the amplification of hypersound in a piezoelectric semiconductor subjected to a static electric field increases the intensity of one of the MB components by a factor of hundreds of thousands when light passes through the crystal at a distance of about 2 mm from the cathode.

Extensive opportunities thus arise for the investigation of various properties of the amplifying materials and also of high-intensity hypersound and the accompanying nonlinear

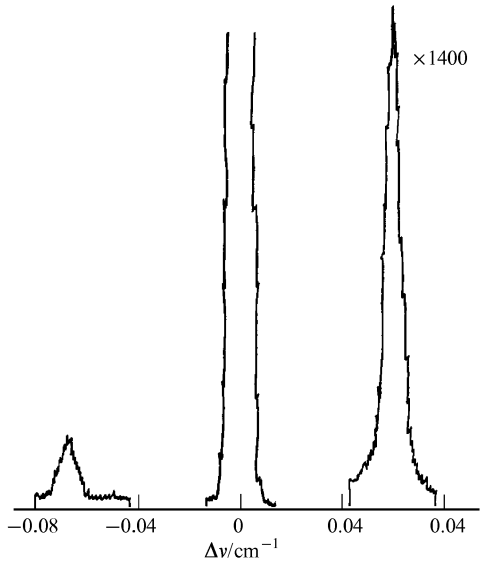

Figure 8. MB spectrum of the piezoelectric semiconductor ZnO in an external static electric field [43].

acoustic phenomena. Some such properties have already been observed [42].

Light scattering at the interface between two media was predicted by Smoluchovsky [2] and observed by Mandelstam [4], who also devised a theory of this phenomenon, which was subsequently developed by Andronov and Leontovich [46]. These first studies involved the use of unresolved light and it was not until 55 years later that the first experimental study of light scattered inelastically by the surface of liquid methane was carried out [47].

The development of spectroscopic studies of light scattered by a surface required devices permitting a marked increase in contrast within the spectrum. A high contrast in the spectrum is necessary in all spectroscopic studies and this was well understood a long time ago. Thus, Dufour [50] was apparently the first to propose the use of one instead of two consecutively arranged interferometers [51], making sure that light passes through it twice. Although the advantages of this scheme have been demonstrated experimentally [52], the low luminosity of the apparatus has prevented wide-scale employment of multipass Fabry–Perot interferometers.

The situation changed radically [49] when laser light sources and improved weakly absorbing dielectric mirrors appeared in the laboratories. Such apparatus has become available in numerous laboratories throughout the world largely owing to the excellent experimental studies by Sandercock [48, 53, 54], who constructed numerous Fabry–Perot interferometers with a corner-cube (triple) prism for the turnback of the light beam and who used his apparatus in a wide variety of investigations.

Multipass Fabry–Perot interferometers are nowadays manufactured in unlimited numbers by companies such as Burleigh and others. This has opened extensive opportunities for research requiring a high contrast of $\sim 10^9 - 10^{12}$ and in particular that involving the determination of the spectra of scattered light modulated by surface waves of various origins. The study of elastic surface and volume waves, propagated in opaque media such as metals and semiconductors, has yielded particularly striking results. In such cases the volume scattering in one direction (into the bulk of a sample) is determined by the depth of a skin layer ($\sim 10^{-6}$ cm) at the optical wavelength of 5×10^{-5} cm and by the cross-sectional area of a light beam on the surface of a sample ($\sim 10^{-2}$ mm^2). Thus the scattering volume is just $\sim 10^{-10}$ cm^3. Furthermore, one must bear in mind that the intensity of the scattered light is maximal in the direction of the reflected light, but one must also not forget that the intensity of the parasitic light, preventing determination of the scattered-light spectrum when the contrast is low, is maximal in the same direction.

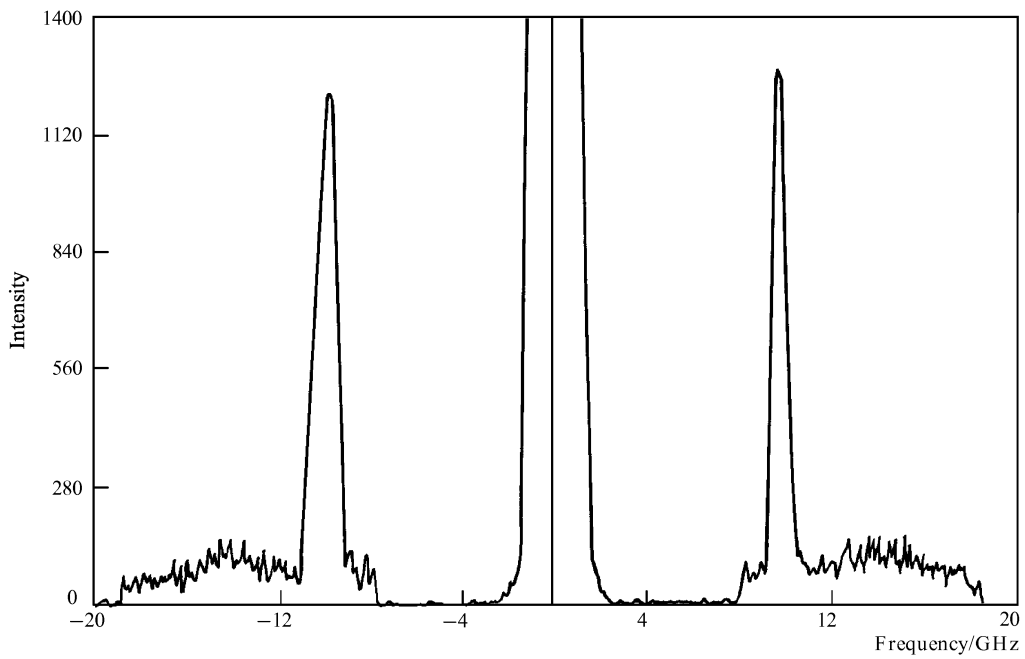

Figure 9. MB spectrum due to a surface Rayleigh wave in a Ge single crystal [60b].

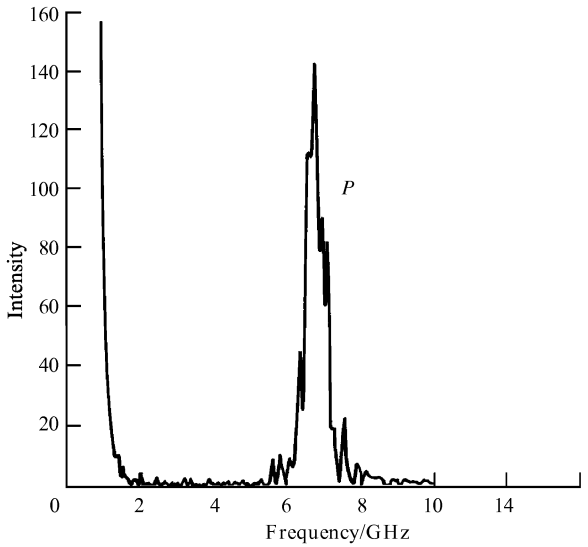

Figure 10. MB spectrum due to a surface Rayleigh wave in a single crystal of the high-temperature superconductor $GdBa_2Cu_3O_{7-y}$. The angle of incidence of light is 55.2° and the scattering angle is 180° [60b].

Good reviews on molecular light-scattering spectra have been written by Fleury [55], Dil [56], Chu [57], Crosignani [58], and Lallemand [71]. Examples of high-precision molecular light-scattering spectra are presented in Figs 9 and 10; they are taken from the papers of Aleksandrov et al. [60]. A multipass Fabry–Perot interferometer is suitable for various experiments and is naturally widely used to solve various problems.

It follows from the examples already presented that molecular light-scattering spectroscopy is effective in the study of various substances and various phenomena under a wide variety of conditions. The method is universal. It affords optical and acoustic information, but one should not imagine that molecular light scattering spectroscopy constitutes a simple and easy way of obtaining fundamental results. This is by no means so. The method requires experimental skill and experience. Major and varied difficulties, which are far from easy to overcome, await the physicist in this field. Perhaps the most significant experimental difficulty is the low intensity of the scattered light. Eqns (2)–(5) and (7) make it possible to estimate the proportion of the exciting light scattered by fluctuations of various origins. It has been found that the proportion of blue exciting light scattered is as follows: $\sim 2 \times 10^{-8}$ in air, $\sim 4 \times 10^{-9}$ in molecular hydrogen, $\sim 10^{-7}$ in a quartz crystal, and $\sim 10^{-5}$ in benzene. Thus, the scattered-light intensity, integrated with respect to frequency, lies in the range from 1×10^{-9} of the intensity of the exciting light for various substances to 1×10^{-5} for liquids such as benzene. The difficulty increases even further when this weak light flux has to be 'spread out' between various frequencies and the spectrum has to be recorded reliably. Another serious difficulty is the need to investigate lines with very different intensities over a narrow spectral range of $\sim 1\ \mathrm{cm}^{-1}$. There are also other difficulties, but we have no space to list them here.

Almost 50 years ago Ginzburg pointed out [61] an interesting MB spectrum of helium II, where (apart from the usual longitudinal sound) yet another type of sound is propagated, so that four MB components should be observed in the spectrum: two due to the longitudinal sound and two due to the second sound. The frequency shift of these components in helium II is $\Delta\omega/\omega \approx 10^{-6}$, for the second sound we have $\Delta\omega/\omega \approx 10^{-7}$, and the overall intensity is 10^{-8} of the intensity of the exciting light. It has been suggested, in particular in my book [11], that this is merely of theoretical interest and that it cannot be observed owing to experimental difficulties. Lasers had only just begun to be used in the laboratory at the time. Vinen and his colleagues [72] disproved my pessimistic views by their detailed spectroscopic investigations and obtained excellent records of the MB components for helium II due to the usual sound and the second sound (Fig. 11). This result must be regarded as a record achievement and my 'prophecy' [11] has proved ill-founded.

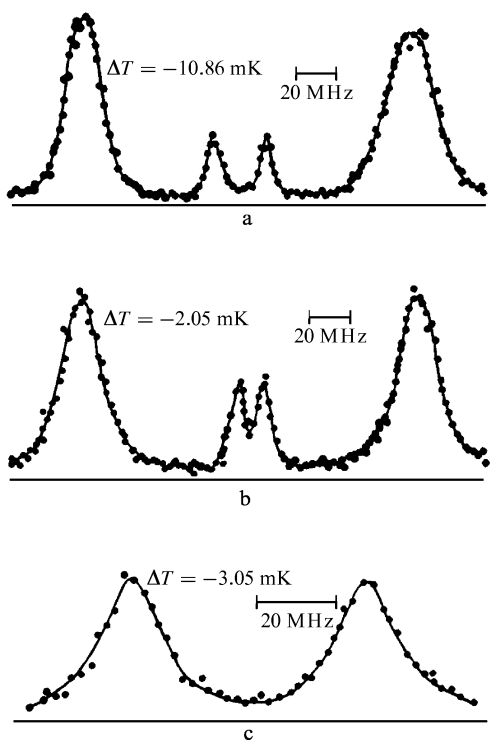

Figure 11. MB spectrum of liquid helium below the λ point (a, b) at a pressure of 20 bar. The inner narrow doublet is due to the second sound. The outer components are due to the first sound (c). The latter spectrum was obtained by reducing the pressure to 17 bar. Only the components due to the first sound can be seen. ΔT is the temperature drop below the λ point. The spectra were recorded by a Fabry–Perot interferometer with plane mirrors separated by 80 cm [72].

The study of the molecular scattering spectra of gases belongs to the class of interesting and important problems. This study has an unusual history, which began 50 years ago (1942) with the experimental search for the MB components in H_2 at 100 atm, in N_2 and O_2 at 80 atm, and in CO_2 at 50 atm [62]. This search was unsuccessful. The components were not recorded and it was actually claimed that the MB components should not exist.

I did not agree with this claim and demonstrated, on the basis of elementary and qualitative considerations, that discrete MB components should be observed for hydrogen, nitrogen, oxygen, and carbon dioxide at the pressures used [62] and for all the investigated gases [63, 64].

If a medium can be regarded as continuous or, in other words, if the mean free path l of a particle of the medium is shorter or, better still, much shorter than the wavelength Λ [Eqn (16)], then all the results referring to liquids in Section 2 apply also to gases, subject only to the condition that the attenuation of the hypersound at a given wavelength is much less than 2π.

If we assume that discrete MB components cannot be observed when the width of a component $\delta\omega = \alpha v$ is equal to the separation between the maxima of the components and the central line,

$$\delta\omega = \Delta\omega = \alpha v = 2n\,\frac{v}{c}\,\omega \sin\frac{\theta}{2}\,, \tag{39}$$

we can obtain the required criterion on the basis of Eqns (16) and (32):

$$\alpha\Lambda = 2\pi\,. \tag{40}$$

Thus, if $\alpha\Lambda \ll 2\pi$, discrete MB components should be observed. The quantity $\alpha\Lambda$ can be estimated from elementary gas-kinetic data:

$$\alpha\Lambda = A\,\frac{\bar{l}}{\Lambda}\,, \tag{41}$$

where a rough estimate yields $A \approx 25$ and this makes it possible to find $\alpha\Lambda$ under experimental conditions when the gas pressure is 50 – 100 bar [11, 64].

If scattered light is observed for $\theta = 90°$ at atmospheric pressure ($\bar{l} \approx 10^{-5}$ cm) and if $\alpha\Lambda > 1$, discrete MB components cannot be observed, but since $\alpha\Lambda < 1$ at just 20 bar discrete components can be observed. This has been confirmed experimentally, although admittedly the first evidence for the existence of a fine structure in gases was obtained under the conditions of stimulated MB scattering (STBS) [65], but the MB components were subsequently also detected in gases due to the scattering by thermal fluctuations [66, 67].

Gases are suitable systems for experimental and theoretical studies if only because different regimes can be realised. For rarefied gases, when $\bar{l} \gg \Lambda$, the gaseous medium cannot be regarded as continuous — each particle scatters the exciting light independently of other scattering centres. The scattering spectrum then reproduces that of the exciting light, but the former is somewhat broader as a consequence of the Doppler shift of the frequency of the scattering centres migrating at thermal velocities. The Maxwellian velocity distribution is assumed. The scattered line half-width is then

$$\delta\omega_{\text{Doppler}} = 2\omega \sin\frac{\theta}{2}\sqrt{\frac{2kT}{mc^2}\ln 2}\,, \tag{42a}$$

where m is the mass of a scattering centre (molecule).

The experimental results can thus be simply described in two extreme cases.

In the intermediate range, when $\bar{l} \approx \Lambda$, it is not difficult to obtain experimental results, but a quantitative theoretical description is no longer quite so simple. Here it is necessary to solve the Boltzmann kinetic equation.

If the changes in the frequency distribution of the intensity $I(\omega)$ are studied at increasing pressures, it can be seen how the Gaussian distribution becomes gradually distorted and, when $\bar{l} \ll \Lambda$, is converted into a distinct triplet in which there are two MB components and a central (Rayleigh) line (see below).

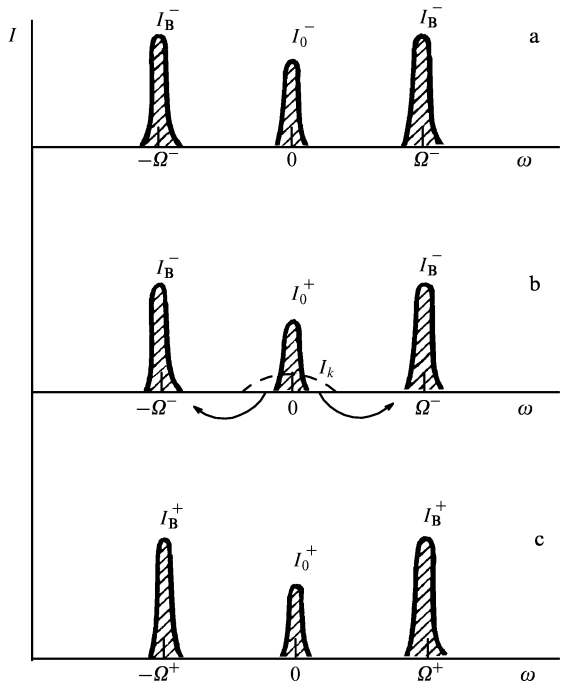

Figure 12. Molecular scattering spectra predicted theoretically for a diatomic gas at various pressures: (a) low gas densities, vibrational degrees of freedom do not participate in the formation of the spectrum; (b) intermediate case, the spectrum has a new component I_k and its integral intensity is $I_0^+ + I_k = I_0$, and the intensity ratio is $I_k/I_0^+ = \frac{2}{7}$; (c) high gas densities, vibrational degrees of freedom taken into account, $I_B^+/I_0^+ = \frac{7}{4}$. In all cases the widths of the components are less than the instrumental width of the spectroscopic instruments [69].

The first experimental study of the spectra of the molecular scattering of light by thermal fluctuations in gaseous Ar, Xe, N_2, CO_2, and CH_4 was carried out by Greytak and Benedek [67] and was followed by other experimental and theoretical investigations [68], in which the changes in the frequency distribution of the intensity as a function of the gas pressure could be readily traced.

Theoretical studies by Andreeva and Malyugin [69] are of special interest: these authors predicted that a new picture of the molecular scattering of light will emerge when all three components can be seen clearly in the scattering spectrum ($\bar{l} \ll \Lambda$).

When account is taken of the interaction of the translational and rotational degrees of freedom and of the dispersion of the kinetic coefficients, a new section appears in the molecular light-scattering spectrum: it represents a narrow band with a maximum at a constant frequency resulting from a redistribution of the intensity in the spectrum (Fig. 12b). At higher pressures the new band is converted into the MB components (Fig. 12c). The redistribution of light in the spectrum is then complete.

The history of investigations of the spectra of light scattered in viscous liquids and glasses has been very similar to the history of such investigations of gases, in the sense that initially the MB components were sought in viscous liquids and glasses, but could not be detected. It was then decided that they should not exist, whereupon they were in fact observed and such studies have continued and have yielded interesting results.

The first investigations were carried out by Gross [73] who observed the MB components in a quartz single

crystal, but he failed to find these components in the spectrum of light scattered by a glass.

The next unsuccessful attempt to observe the MB components in glasses was made by Ramm [74]. Other attempts to detect these components in the spectrum of light scattered by glasses and viscous liquids were likewise unsuccessful [75–78]. The studies were of a fundamental nature and the results seemed to be so reliable that it became desirable to explain this and such an explanation was in fact formulated [78]. Briefly the explanation is as follows: it is well known that the half-width $\delta\omega$ of the MB components is determined by the absorption coefficient of hypersound [Eqn (32)] and this coefficient is proportional to the viscosity: $\alpha \propto \eta$ [Eqn (33)]. Next it is claimed that the viscosity of highly viscous liquids and glasses is enormous and reaches $\sim 10^{18}$ P.

The viscosity measured under static conditions is indeed as high as this and, according to Rank and Douglas [78], its enormous value broadens the MB components so much that they cannot be observed as discrete lines. If a viscosity of $\sim 10^{18}$ P determines the absorption of sound in glasses, then even a thin glass layer should not transmit sound waves. However, it is well known that this is not the case and that even hf sound passes through glass readily. The important point is that, even at low sound frequencies, the relaxation process renders the absorption of sound incomparably weaker than might have been expected on the basis of the viscosity at zero frequency. The relaxation process also leads to the dispersion of the velocity of sound [11, 29].

This lack of knowledge or misunderstanding of the role of relaxation has been largely responsible for the long-lasting failure to observe the MB components in viscous liquids and glasses. All the above-mentioned experimental searches for these components in viscous liquids and glasses [73, 78] were carried out before laser light sources became available in laboratories and for this reason the exposures lasted many hours and even many tens of hours.

For a long time it has been unclear why, for example, the MB components are clearly seen in glycerol at 50–60 °C, while in the region of the glass-transition temperature T_g of the same glycerol it has not been possible to find these components.

If one bears in mind that the relaxation process results in the dispersion of the velocity of sound and that at high viscosities and high hypersonic frequencies it can reach 100%, the velocity of sound is doubled. This means that the adiabatic compressibility β_S decreases by a factor of 4 and the integral MB component intensity [Eqn (2)] also decreases by the same factor. Consequently, the exposure must also be increased by a factor of 4. Under such conditions, exposures lasting many hundreds of hours are needed to observe these components.

When this became understood, Pesin and I [79, 80] increased the aperture ratio of our apparatus by an order of magnitude and discovered the MB components for a number of viscous media. Krishnan [81] was the first to observe these components in fused quartz at 300 °C at the $\lambda = 2636$ A line in apparatus with a mercury vapour resonance filter. Stoicheff et al. [82] also detected the MB components related to longitudinal and transverse hypersound in fused quartz: they used a lamp operating on the basis of the mercury-198 isotope. These problems were examined in greater detail in my book [11].

In all these cases it has been assumed that the scattering medium is at an equilibrium temperature identical at all points within the medium.

Almost 60 years ago, Mandelstam [85] stated that if there is a temperature gradient, the intensity of light scattered at a particular point within a body depends on the temperature at other points in the body. The distribution of the scattered-light intensity is then more uniform than the temperature distribution. Mandelstam [85] predicted that this may be observed in solids and in liquids, while according to Andreeva and Malyugin [69] this phenomenon with its interesting features should also be observed in gases at suitable pressures.

The theory of the phenomenon predicted by Mandelstam [85] for solids and liquids was developed quantitatively by Leontovich [86]. The physical nature of the phenomenon can be readily understood if one takes into account the fact that the scattering of light may be regarded as diffraction by a Fourier component; for example, by an adiabatic fluctuation or an elastic thermal wave with a wave vector $\pm\boldsymbol{q}$. A maximum of the scattered (diffracted) light is observed for exciting light with a wavelength λ at an angle θ when condition (16) is fulfilled (Fig. 1). Fluctuations at the most diverse points within a given body generate an elastic wave with a wave vector $\boldsymbol{q}$. Therefore, if a body is heated nonuniformly, elastic waves or Fourier components with different amplitudes arrive at the point of observation of the scattered light. For this reason, if the wave with $-\boldsymbol{q}$ differs in amplitude from the wave with $+\boldsymbol{q}$, the intensity of the Stokes MB-scattering component also differs from that of the anti-Stokes component.

Thus, in the presence of a steady temperature gradient, the scattering at a particular 'point' in a sample depends also on the temperature of the neighbouring regions. The effect depends on the shape and size of a sample, as pointed out by Mandelstam in his very first communication [85]. Mandelstam also mentioned that the distribution of the scattered-light intensity does not reflect exactly the temperature distribution because the Debye waves, responsible for light scattering, are attenuated only very weakly and their energy constitutes a very small proportion of the energy corresponding to the entire Debye spectrum.

The first attempt to investigate experimentally the scattering of light in a nonuniformly heated body was made by Landsberg and Shubin [87], who investigated the scattering in a nonuniformly heated quartz single crystal illuminated with white light. Within the limits of an experimental error of $\sim 1\%$, Landsberg and Shubin [87] found no deviation of the intensity distribution from that for a uniformly heated body, which enabled them to conclude that the absorption coefficient is $\alpha > 0.75\,\mathrm{cm}^{-1}$ for the elastic waves responsible for the light scattering. On the other hand, since the discrete Brillouin components are observed in a quartz crystal, one can postulate that $\alpha < 5 \times 10^4\,\mathrm{cm}^{-1}$.

Another interesting opportunity for an experimental study of the scattered light in the presence of a temperature gradient in a sample was indicated by Vladimirskii [88]. It is based on the fact that light scattered (diffracted) by thermal waves travelling along and opposite to the temperature gradient has different amplitudes, so that the Stokes and anti-Stokes components have different intensities.

According to Leontovich [86], the asymmetry of the intensities of the MB components can be formulated as

follows:

$$\frac{I_s - I_{as}}{I} = \frac{\nabla T \cos\vartheta_B}{\alpha T} , \tag{42b}$$

where I_s and I_{as} are the intensities of the Stokes and anti-Stokes MB-scattering components, I is the intensity of the scattered light in the absence of a gradient, T is the temperature at the test point within the medium, and ϑ_B is the angle between the direction of the temperature gradient and the direction of propagation of an elastic thermal wave.

An experiment designed to observe the asymmetry of the intensities of the MB components of light scattered in an yttrium aluminium garnet (Y_3AlO_{12}) in the presence of a steady temperature gradient was undertaken by Chistyi [89], who described his study in detail. The asymmetry of the MB intensities was not observed in this investigation either.

It follows from the foregoing that, starting from 1934, the phenomenon has constantly attracted the attention of theoretical and experimental physicists and its theory has been sufficiently complete to obtain significant characteristics of the scattering medium from experimental data. However, the experiments undertaken did not yield the expected result. I described all this interesting history of the problem in fair detail (with the exception of Chistyi's work [89]) in my book [11] published in our country in 1965 and in an English translation in the USA in 1968. It appears that, quite independently of Leontovich's studies [86] described above, several theoretical investigations of fluctuations in a nonequilibrium medium and in particular of the scattering of light by these fluctuations were undertaken [90] and the expression obtained for the asymmetry of the MB components in the presence of a temperature gradient agreed with that predicted [Eqn (42a)] by the 50-year-old Leontovich theory [11, 86].

Studies were then published by authors familiar with the early theoretical and experimental investigations [83, 91–93]. This account naturally does not cover all the theoretical investigations in this field.

A qualitative observation of the asymmetry of the MB components of the scattering in liquid water in the presence of a temperature gradient $\nabla T = 100\,\mathrm{K\,cm^{-1}}$ has been reported [94].

Subsequently Kiefte, Clouter, and Penney [95] quantitatively determined the asymmetry of the MB components in the presence of a temperature gradient in water and in fused quartz.

The asymmetry of the MB components predicted by the theory [95] can be formulated as follows:

$$\varepsilon = \frac{v}{2\Gamma T}\frac{(\boldsymbol{q}\cdot\nabla T)}{q^2} , \tag{42c}$$

where

$$\varepsilon = \frac{I_s - I_{as}}{I_s + I_{as}} ,$$

v is the velocity of sound; Γ and $\boldsymbol{q}$ are defined by Eqns (20) and (13). Eqn (42b) is transformed into Eqn (42c) if account is taken of Eqns (20) and (31)–(34).

Fig. 13 is a schematic diagram of the apparatus used by Kiefte et al. [95]. In this apparatus, the scattered light was observed at an angle of $\sim 1^\circ$ and was analysed with the aid of a confocal Fabry–Perot interferometer. The

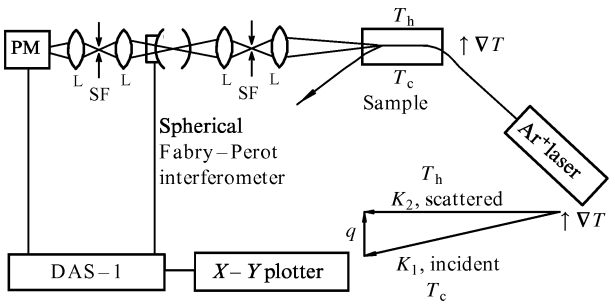

Figure 13. Schematic diagram of the apparatus used in determination of the MB spectrum of a medium with a constant temperature gradient [95]. Here, PM is a photomultiplier.

temperature gradient was varied in the range 0–45 K $\mathrm{cm^{-1}}$ at temperatures of 288–307 K. The dependence of the Jasymmetry of the intensity of the MB components on $\boldsymbol{q}\cdot\nabla T/q^2$ is illustrated in Fig. 14.

The correlation function $C(T, q)$, describing the central or Rayleigh line in the presence or a steady temperature gradient ∇T, was subsequently calculated on the basis of a theory of the interacting modes of diffusional and viscous motions.

The correlation function obtained has the following form:

$$C(t, q) = C_b\left\{1 + C_0\left[\left(1 + \frac{A\eta}{\rho}\right)\exp(-Dq^2T) - A\exp\left(-\frac{\eta}{\rho}q^2T\right)\right]\right\} ,$$

where

$$A = B\frac{(\nabla T)^2}{q^4} , \quad B = \frac{C_P}{T[(\eta/\rho)^2 - D^2]} ,$$

C_b defines the background against which the correlation function is observed, C_0 is the correlation function for $\nabla T = 0$, and T is the average absolute temperature.

The experiments show that the theoretical predictions described above agree with experimental results for a liquid [96].

4. Spectroscopic investigations of the central (Rayleigh) line in the scattered-light spectrum

The spectra of light scattered by adiabatic fluctuations of the density or of the pressure are considered above. I shall now discuss isobaric fluctuations of the density or of the entropy ΔS or of the temperature ΔT.

This topic has been the subject of various theoretical investigations concerned with a range of media [11, 83, 84, 96–98]. Fluctuations of the entropy in liquids and solutions will now be considered, but the conclusions reached are fully applicable to all types of media within the hydrodynamic approximation.

As in the case of adiabatic fluctuations of the density, the spectral singularities of the light scattered as a result of the entropy fluctuations are governed by the law of modulation of the light scattered by the time-dependent fluctuations of the entropy, temperature, or concentration (if a solution is considered).

The entropy or temperature fluctuations appear and disperse at a rate governed by the thermal diffusivity χ of a

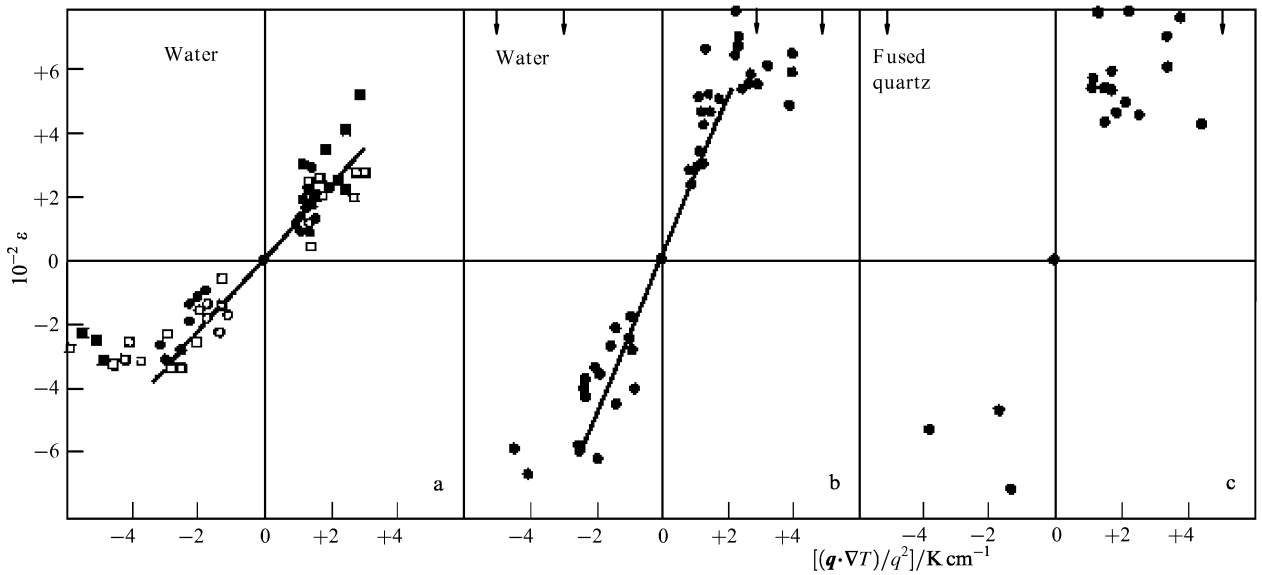

Figure 14. Dependence of the asymmetry of the intensities of the MB components on $\nabla T/q^2$: (a) various data for water, $\nabla T = 17-40\,\mathrm{K\,cm^{-1}}$ and $T = 288$ K (open circles), 293 K (black circles), 298 K (open squares), and 303 K (black squares); $\nabla T = 28.3\,\mathrm{K\,cm^{-1}}$ and $T = 296$ K; (b) 'best' results for water with $\nabla T = 45\,\mathrm{K\,cm^{-1}}$ and $T = 307$ K, the outer arrows in the upper part of the figure correspond to $q = 3000\,\mathrm{cm^{-1}}$ and the inner arrows correspond to $4000\,\mathrm{cm^{-1}}$; (c) data obtained for fused quartz, $\nabla T = 80\,\mathrm{K\,cm^{-1}}$ and $T = 315$ K, the arrow at the top corresponds to $q = 4000\,\mathrm{cm^{-1}}$ [95].

given medium or by the diffusion coefficient D if the medium is a solution. The nature of the time dependence of the rms fluctuations of the entropy (temperature) is described by the well-known Fourier equation or by the heat conduction equation. If we assume the previously discussed time dependence of an optical inhomogeneity described by $\langle\Delta n^2\rangle^{1/2}$, $\langle\Delta S^2\rangle^{1/2}$, $\langle\Delta T^2\rangle^{1/2}$, $\langle\Delta C^2\rangle^{1/2}$, and if we postulate that $\langle\Delta n^2\rangle^{1/2}$ is described by $\Phi(t)$, we can write the Fourier equation in the following form [11]:

$$\dot{\Phi} - \chi\nabla^2\Phi = 0 \ . \tag{43}$$

We shall seek the solution of Eqn (43) in the usual form

$$\Phi(t) = \Phi_0 \exp[\mathrm{i}(mt - \boldsymbol{q}\cdot\boldsymbol{r})] \ .$$

Substitution of this solution into Eqn (43) gives

$$\Phi(t) = \Phi_0 \exp(-\delta_\mathrm{s} t)\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}) \ , \tag{44}$$

where

$$\delta_\mathrm{s} = q^2\chi \tag{45}$$

and

$$\chi = \frac{\kappa}{C_P\rho} \ . \tag{45$'$}$$

Here, κ is the thermal conductivity and C_P is the specific heat at constant pressure.

It follows from Eqn (44) that the resultant fluctuations $\langle\Delta S^2\rangle^{1/2}$ and $\langle\Delta T^2\rangle^{1/2}$ disperse in accordance with an exponential law and the rate of dispersal or the spreading time $\tau_\mathrm{s} = 1/\delta_\mathrm{s}$ is governed by the constant χ and by the wave number q. By way of example, it is assumed that $\lambda = 5\times10^{-5}$ cm and $\chi = 10^{-3}\,\mathrm{cm^2\,s^{-1}}$, then at $\theta = 90$ °C, the spreading time is $\tau_\mathrm{s} \sim 10^{-8}$ s. The scattered-light field, modulated by Eqn (44), is then

$$E(t) = E_0\Phi_0 \exp(-\delta_\mathrm{s} t)\exp(\mathrm{i}\omega t) \ , \tag{46}$$

which leads to the following time dependence of the scattered-light intensity

$$I(t) = I_0 \exp(-2\delta_\mathrm{s} t) \ . \tag{47}$$

It follows from Eqn (47) that the light scattered by the entropy fluctuations decays exponentially without oscillations of the kind observed for the adiabatic fluctuations described by Eqn (17).

Since the concentration fluctuations $\langle\Delta C^2\rangle^{1/2}$ disperse in accordance with the same law as $\langle\Delta S^2\rangle^{1/2}$, it follows that the nature of the solution and the subsequent expressions should be the same as for $\langle\Delta S^2\rangle^{1/2}$ if χ is replaced with the diffusion coefficient D, so that the function modulating the scattered light is

$$\Phi(t) = \Phi_0 \exp(-\delta_\mathrm{c} t)\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}) \ , \tag{48}$$

where

$$\delta_\mathrm{c} = q^2 D \ . \tag{49}$$

In one of his early papers Mandelstam [17] considered the fluctuations of the temperature and concentration, and derived Eqn (47). He discussed [17] the process leading to the appearance of an unshifted line in the scattered-light spectrum. The distribution of the intensity on the frequency scale of such a line can be obtained by expanding $E(t)$ as a Fourier integral and then calculating the scattered-light intensity as a function of the frequency. This is exactly the procedure adopted above in Eqns (25)–(30) and the final result is

$$I_\mathrm{s}(\omega) = \frac{(\delta_\mathrm{c}/\pi)I_\mathrm{is}}{\omega^2 + \delta_\mathrm{s}^2} \ . \tag{50}$$

The total intensity of the central component I_is is

$$\int_{-\infty}^{\infty} I_\mathrm{s}(\omega)\,\mathrm{d}\omega = I_\mathrm{is} \ , \tag{51}$$

where I_is is given by Eqn (3).

The half-width of this line at half-amplitude $I_s(\omega)/2$ is then

$$\delta_s = \delta\omega_s = q^2\chi \ . \tag{52}$$

Here, q is given by Eqn (13).

In the same way we can obtain the intensity $I_c(\omega)$ of the light scattered as a result of the concentration fluctuations:

$$I_c(\omega) = \frac{(\delta_c/\pi)I_c}{\omega^2 + \delta_c^2} \ , \tag{53}$$

where I_c is described by Eqn (4) and the line half-width at half-amplitude $I_c(\omega)/2$ is

$$\Gamma = \delta\omega_c = q^2 D \ . \tag{54}$$

An estimate of the time needed to establish the spectrum of light scattered by the concentration fluctuations, obtained on the assumption that $D = 10^{-5}\,\mathrm{cm^2\,s^{-1}}$ and that the conditions are the same as in the preceding example, gives $\tau_c \sim 10^{-6}$ s. The Einstein expression for the mutual diffusion coefficient D is

$$D = \frac{kT}{6\pi\eta r} \ , \tag{55}$$

where η is the shear viscosity and r is, strictly speaking, the radius of a macroscopic particle.

Einstein also applied this expression to molecules, but the result is physically meaningless and can be justified only by the success of expression (55) in the case of molecular systems.

The half-width of the central (Rayleigh) line for the scattering in a one-component medium or in a solution can be described by a general expression of the following type:

$$\delta\omega = \frac{L}{\chi^*} \ , \tag{56}$$

where L are the Onsager kinetic coefficients and χ^* is the generalised susceptibility.

In the critical range the value of L is practically independent of temperature, whereas χ^* increases strongly because of the critical opalescence [99 – 104] and, therefore, the central line half-width tends to zero. Therefore, a reduction in the half-width of the Rayleigh scattered-light line and an increase in its intensity are due to the same cause which is an increase in the correlation radius of the concentration fluctuations in a solution or of the density fluctuations in a one-component liquid because of approach to the critical point.

Expressions (5) and (7) derived for the intensity of the scattered light are inapplicable to the case when the temperature of a liquid or a solution is close to the critical temperature. Expressions (5) and (7) are derived on condition that the fluctuations are independent of one another. In the region of the critical temperature this condition is not satisfied. In the critical region the fluctuations influence one another at effective distances r_c, which can be called the correlation radii. This important point was allowed for by Ornstein and Zernike [105] who generalised expressions (5) and (7) to the critical range of temperatures. This generalisation by Ornstein and Zernike leads to the following expression for the intensity of the scattered light I_{0Z}:

$$I_{0Z} = I(1 + q^2 r_c^2)^{-1} \ , \tag{57}$$

where I is given by Eqns (5) or (7). In the limiting case of long-wavelength harmonics ($q \to 0$), we find that (57) reduces to the initial expressions (5) and (7). The dependence of I_{0Z}^{-1} on q^2 is a straight line, the slope of which makes it possible to find r_c^2. In this method the determination of r_c requires finding first the dependence of the relative intensity on the scattering angle or, equivalently, on q. This has been done on many occasions (see, for example, Refs [11, 102, 107 – 109] and the literature cited there).

Another method for determination of the correlation radius of the entropy, temperature, or concentration fluctuations is purely spectroscopic. It basically involves determination of the width of the Rayleigh line in the scattered-light spectrum. The first determination of the Rayleigh line width in the critical region was reported by Alpert, Yeh, and Lipsworth [110], but since then there have been extensive and multifaceted theoretical investigations [11, 102 – 109]. A brief account will not be given of some results of the studies of critical solutions which have a double critical point. Systems of this kind have been largely neglected, although they are of considerable interest for the understanding of the physical features of phase transitions in general [111].

The phase diagrams of some binary solutions represent a crater-like surface when plotted in terms of the coordinates temperature T and concentration C. Inside such a crater the components of the solution become separated. The minimum of the crater corresponds to a double critical point (Fig. 15).

There are many solutions with the upper critical point: by way of example, we can mention nitrobenzene – hexane, aniline – cyclohexane, nitroethane – trimethylpentane, and many others. A crater-like phase diagram with its extremum at T_{cL} and C_L has the lower critical point. By way of example, we can mention trimethylamine – water, gamma – collidine – water, lutidine – water. There are fewer solutions with the lower critical point. There are also certain systems which, described in terms of the coordinates T and C, form closed regions or loops inside which the compo-

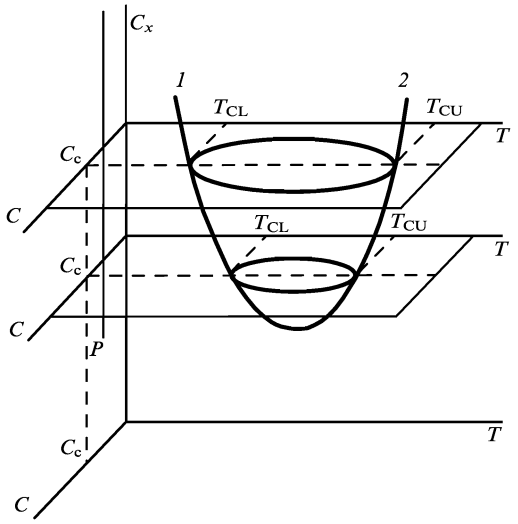

Figure 15. Phase diagram with a crater-like phase separation surface (C_x is the concentration of the third component): (*1*) line of lower critical points; (*2*) line of upper critical points. The surface minimum corresponds to the double critical point (which is the point where lines *1* and *2* meet) [111].

nents of the binary solution become separated and the positions of the separate phases are stable.

The last type of phase diagram appears only if a small amount ($\sim 0.5\% - 1.0\%$) of the third component is added to a binary system. For example, water may be added to a guaiacol–glycerol solution, Na_2SO_4 to a β-picoline–water solution, and salt to an OH–propanol–water solution. There are relatively few such solutions and they have been studied less thoroughly. The greater the amount of water in a guaiacol–glycerol solution, the larger the region where guaiacol and glycerol do not form a solution, but are in separate stable phases.

Systems of this kind simultaneously possess the upper and lower critical points (represented by horizontal sections of the crater in Fig. 15).

Since the nature of the phase diagram depends strongly on the amount of the added third component, a three-dimensional phase diagram can be constructed, as is done for a guaiacol–glycerol solution in Fig. 15. In this figure the vertical axis gives C_x, which is the concentration of water. The other two coordinates are the temperature and the concentration of guaiacol in glycerol.

The phase diagram is then a crater-like surface and the upper and lower critical points are transformed into lines of such points. The double critical point is where the lines of critical points meet at the extremum.

As pointed out earlier, the half-width of the central (Rayleigh) line in the scattered-light spectrum is equal to the product of the square of the wave number and the mutual diffusion coefficient, as given by Eqn (54). It follows from Eqn (55) that the diffusion coefficient is itself a function of temperature, as well as of the shear viscosity and of the size r, which in the critical region should differ greatly from the size of a molecule and which represents the correlation radius of the concentration fluctuations.

Extensive experimental and theoretical investigations have ben made of phase transitions and critical phenomena in various media under diverse conditions [32–36, 38, 97, 98, 100–102, 106, 107, 112, 113]. There have also been many attempts to develop a theory of phase transitions and critical phenomena of solutions that exhibit phase separation. Here, I shall mention primarily the papers that have led to the development of a theory of interacting modes [97, 98, 100, 101, 114–119]. This theory accounts well for the experimental results and describes the half-width of the central line in the spectrum representing the concentration fluctuations by the expression

$$\Gamma = \Gamma_{\mathrm{B}} + \Gamma_{\mathrm{c}} = D_{\mathrm{B}} q^2 (1 + x^2) + D_{\mathrm{c}} R q^2 K(x) \ . \tag{58}$$

The subscripts B and c indicate that the quantity is divided into the background (B) and critical (c) parts; q is the wave number of the scattered light; $x = qr_{\mathrm{c}}$, where r_{c} is the correlation radius of the concentration of fluctuations; $R = 1.027$; $K(x)$ is a function of the following type [120, 121]:

$$K(x) = \frac{3}{4} x^{-2} [1 + x^2 + (x^3 - x^{-1}) \arctan x] \ . \tag{59}$$

The background D_{B} and critical D_{c} values predicted by this theory [115, 116, 122] are

$$D_{\mathrm{c}} = \frac{kT}{6\pi\eta r_{\mathrm{c}}} \ , \tag{60}$$

$$D_{\mathrm{B}} = \frac{kT}{16\eta_{\mathrm{B}} r_{\mathrm{c}}} \frac{1}{q r_{\mathrm{c}}} \ . \tag{61}$$

Here, η is the shear viscosity and its background component is η_{B}. The value of q_{c} can be found from [122]

$$Q_0^{-1} = 2 q_0^{-1} \exp\left(-\frac{4}{3}\right), \quad q_0^{-1} = q_{\mathrm{c}}^{-1} + q_{\mathrm{D}}^{-1} \ ; \tag{62}$$

q_{D} and Q_0 are quantities with the dimensions of the wave number. Q_0 can be obtained from the temperature dependence of the shear viscosity [122]

$$\frac{\eta}{\eta_{\mathrm{B}}} = (Q_0 r_{\mathrm{c}})^{x_\eta} \ . \tag{63}$$

Here, x_η is the critical exponent of the viscosity and q_{D} is a finite number, but such that the theory based on the approximation of a continuous medium is applicable. It therefore follows from expressions (58)–(63) predicted by this theory that measurements of all the quantities in these expressions (with the exception of r_{c}) can be used to find r_{c} and its temperature dependence, as was done for the guaiacol–glycerol solution [123]. If r_{c} is written in terms of the dimensionless temperature [124], the following expression can be used:

$$r_{\mathrm{c}} = r_0 (\varepsilon_1 \varepsilon_2)^{\nu} \ , \tag{64}$$

where

$$\varepsilon_1 = \frac{T_{\mathrm{c}}^{\mathrm{L}} - T}{T_{\mathrm{c}}^{\mathrm{L}}} \ , \quad \varepsilon_2 = \frac{T_{\mathrm{c}}^{\mathrm{U}} - T}{T_{\mathrm{c}}^{\mathrm{U}}} \ .$$

Here, $T_{\mathrm{c}}^{\mathrm{L}}$ and $T_{\mathrm{c}}^{\mathrm{U}}$ are the lower and upper critical temperatures of the guaiacol–glycerol mixture, r_0 is a constant, and ν is the critical component.

This investigation has established that if $\Delta T = T_{\mathrm{c}}^{\mathrm{U}} - T_{\mathrm{c}}^{\mathrm{L}} > 1.5$ °C, the critical exponent is 0.631 ± 0.094 in agreement with Ref. [128] and our earlier measurements [125, 126]. This result fits within the framework of the fluctuation theory, but if the phase separation region corresponds to $\Delta T < 1.5$ °C, the value of ν decreases tending to $\nu = 0.5$ as predicted by the Landau theory. This result is somewhat unexpected.

In the direct vicinity of the double critical point the experimental value of the critical exponent [123] is $\nu = 1.02 \pm 0.01$, although one would expect $\nu = 1.26$ (for details see Ref. [123]).

An extensive theoretical investigation of some of the systems with the double critical point was reported in Ref. [127]. This purely theoretical paper describes phase diagrams and gives a physical explanation of the existence of the upper and lower critical points on the basis of the strength of the hydrogen-bonding force.

However, it seems that the physical origin of the lower critical point needs new studies and convincing arguments to ensure the correct understanding of the nature of the phenomena involved.

Experimental studies of guaiacol–glycerol solutions have revealed several surprising effects. For example, if such a solution is carefully purified to remove water, it becomes homogeneous in terms of the coordinates T and C for any value of T and C. Only the addition of about 0.5% of water causes the solution components to separate in a certain region and the greater the amount of water the greater this region, but it is sufficient to add, for example,

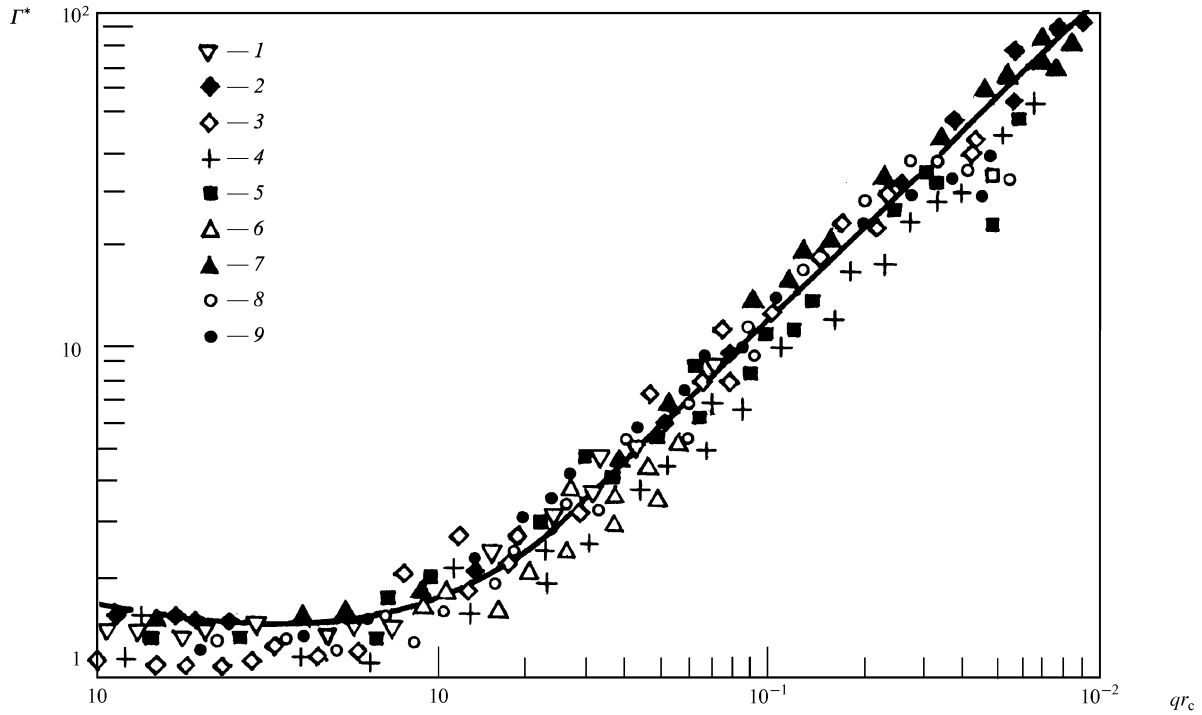

Figure 16. Dependence of the reduced half-width Γ^* of the Rayleigh line on qr_c for various systems: (*1*) nitroethane-3-methylpentane; (*2*) isobutyric acid – water; (*3*) aniline – cyclohexane; (*4*) 2,6-lutidine – water; (*5*) SF_6 (ρ_c); (*6*) CO_2 (coexistence curve); (*7*) CO_2 (ρ_2); (*8*) Xe (coexistence curve); (*9*) Xe (ρ_c) (see Ref. [71]).

ethanol to such a solution in amounts smaller than that of water to induce disappearance (collapse) of the phase separation region, so that the solution is again homogeneous.

In the theoretical treatment given in Ref. [127] it is stated that the nature of the lower critical point depends strongly on the behaviour of the strength of the hydrogen-bonding forces in the vicinity of this point.

However, our experimental investigation [128] had shown that the strength of the hydrogen-bonding forces behaves differently in the regions of the upper and lower critical points. This could be used as the support of the hypothesis put forward in Ref. [127]. However, the following new important evidence has been obtained recently.

If a small amount of benzene of CCl_4 (each substance is free of hydrogen bonds) is added to a initially 'dry' homogeneous solution, a separation region appears in this solution. The question therefore arises whether the hydrogen-bonding forces are important here or are we dealing with something else?

Ethyl alcohol, which does not induce a phase separation region and can even suppress it if it is induced by the presence of water, dissolves well in both components of the solution, whereas water dissolves in just one component (glycerol), and benzene and CCl_4 also dissolve in one component (guaiacol).

This whole phenomenon has to be investigated in greater detail experimentally. A solution with a double critical point and, in particular, a guaiacol – glycerol solution represents a special object which is very sensitive to the intermolecular interactions and, therefore, can be studied experimentally more readily than other objects. If the cases about which there is little experimental evidence are excluded, it is found that the theory of interacting modes describes well the great variety of accumulated experimental data.

A comparison of the theoretical expressions with these data is made by deriving the following dimensionless quantity (width) from Eqn (58):

$$\Gamma_c^* = \frac{6\pi\eta}{kT}\frac{\Gamma_c}{q^3}$$

and plotting this quantity as a function of qr_c and then superimposing the experimental values on the continuous curve obtained in this way [129].

Fig. 16 shows how well the theory fits the experimental results.

5. Spectrum of depolarised scattered light

A polarisation analysis shows that the scattered light consists of linearly polarised light, scattered by optically isotropic inhomogeneities resulting from fluctuations of — for example — the density and entropy, and depolarised light scattered by anisotropic inhomogeneities due to fluctuations of the anisotropy.

The depolarisation of scattered light was discovered a long time ago. The first results were reported by Tyndall (1869) and were obtained in a study of the polarisation of light scattered by small solid particles. This has been confirmed by studies of light scattered by the terrestrial atmosphere and finally, much later, by investigations of light scattered in gases, liquids, and solids.

5.1 Estimate of the integral intensity of light scattered as a consequence of anisotropy fluctuations

The integral intensity of light scattered as a result of fluctuations of the anisotropy of liquids frequently exceeds

the intensity of light scattered as a consequence of isotropic fluctuations [11].

Let us assume that a parallel beam of natural light propagates along the x axis and that an isotropic optical inhomogeneity (fluctuation) is located at the origin of the coordinate system. The exciting light induces a moment P in the inhomogeneity and the scattered-light field can be described by $E' \propto \Delta\varepsilon\ddot{P}$, where $\Delta\varepsilon$ is a scalar, and therefore the electric vector of the light wave E' is parallel to P or, in other words, only linearly polarised light is present, irrespective of whether the exciting light is natural ($E_z = E_y$) or linearly polarised (E_z). In this case and those discussed later the scattered light is observed along the y axis at 90° to the direction of the exciting light. In this geometry, illumination of an inhomogeneity by linearly polarised light with $\boldsymbol{E} = E_y$ produces no scattered light along the y axis.

If an anisotropic inhomogeneity is located at the origin of the coordinate system, the induced moment P does not coincide in the direction with E_z and we have $E'_i \propto \Delta\varepsilon_{ik}E_i$, where $\Delta\varepsilon_{ik}$ is a tensor and the scattered light has two components E'_z and E'_x; this results in depolarisation of the scattered light.

A measure of this depolarisation is the depolarisation coefficient described as the ratio

$$\frac{|E'_x|^2}{|E'_z|^2} = \frac{I_x}{I_z} .$$

The indices x and z are usually replaced with H, when the position of the electric field vector is horizontal (in the scattering plane), and with V, when this vector is vertical (perpendicular to the scattering plane). Two such indices are employed and the first refers to the direction of $\boldsymbol{E}$ in the exciting light and the second to the position of $\boldsymbol{E}$ in the scattered light.

If the intensity of the polarised scattered light is denoted by $I = I_{\mathrm{VV}}$ and the intensity of the depolarised scattered light is $i = i_{\mathrm{VV}} + i_{\mathrm{VH}}$, the depolarisation coefficient of the total scattered-light flux, which for $\theta = 90°$ is

$$J = I_{\mathrm{VV}} + i_{\mathrm{VV}} + i_{\mathrm{VH}} , \tag{65}$$

is described by the expression

$$\Delta_{\mathrm{u}} = \frac{i_{\mathrm{VH}}}{I_{\mathrm{VV}} + i_{\mathrm{VV}}} , \tag{66}$$

and the depolarisation coefficient of the light scattered by the anisotropy fluctuations is

$$\rho = \frac{i_{\mathrm{VH}}}{i_{\mathrm{VV}}} . \tag{67}$$

Elimination of i_{VV} and i_{VH} from Eqn (65) by means of Eqns (66) and (67) gives

$$J = I_{\mathrm{VV}} \frac{\rho(1+\Delta)}{\rho - \Delta} . \tag{68}$$

According to the theory and in full agreement with experiments (see Ref. [11] and the literature cited there), when the exciting light is natural, then $\rho = 6/7$, and for the excitation with linearly polarised light, the corresponding value is $\rho = 3/4$.

The expression given by the fraction in Eqn (68) is known as the Cabannes factor because Cabannes was the first to allow for the integral intensity of light scattered because of the anisotropy fluctuations.

If $\rho = 6/7$, this factor is

$$f(\Delta) = \frac{6 + 7\Delta}{6 - 7\Delta} ,$$

but for $\rho = 3/4$, it becomes

$$f(\Delta) = \frac{3 + 3\Delta}{3 - 4\Delta} .$$

The total intensity of the molecularly scattered light when the scattering angle is $\theta = 90°$ can therefore be found if expressions (2)–(5) and (7) are multiplied by $f(\Delta)$.

The relationships given above readily yield the ratio of the integral intensity i of light scattered by the anisotropy fluctuations to the intensity I of light scattered by the density fluctuations:

$$B = \frac{i}{I} = \frac{\Delta(1+\rho)}{\rho - \Delta} . \tag{69}$$

If the exciting light is natural, then $\Delta = \Delta_{\mathrm{u}}$ applies to this exciting light and we again have $\rho = 6/7$, but if the exciting light is linearly polarised and the vector $\boldsymbol{E}$ is perpendicular to the scattering plane, then $\Delta = \Delta_{\mathrm{V}}$ and $\rho = 3/4$. The relationship between Δ_{u} and Δ_{V} is

$$\Delta_{\mathrm{u}} = \frac{2\Delta_{\mathrm{V}}}{1 + \Delta_{\mathrm{V}}} , \quad \Delta_{\mathrm{V}} = \frac{\Delta_{\mathrm{u}}}{2 - \Delta_{\mathrm{u}}} . \tag{70a}$$

If the exciting light is natural, it follows from measurements that $B = 1.92$ for benzene, 5.15 for carbon disulfide, 13 for salol and benzophenone. In other words, the intensity of light scattered by the anisotropy fluctuations in these substances can exceed the intensity of light scattered on the density fluctuations by a factor of 2, 5, or even an order of magnitude. For substances such as acetone we have $B = 0.56$, for ethyl ether we have 0.20, and for carbon tetrachloride it is 0.12, so that for these substances the intensity of light scattered by the anisotropy fluctuations is much less than the intensity of light scattered by the density fluctuations. The ratio (69) makes it possible to estimate the value of B for any substance.

5.2 Spectrum of depolarised light scattered in liquids

The depolarised light scattered by the anisotropy fluctuations has been discovered in the spectrum of scattered light in the form of a fairly wide band with a maximum which coincides with the position of the frequency of the exciting light and which falls on either side, but extends by 100–150 cm^{-1} or further and is usually called the wing of the Rayleigh line.

This effect was discovered simultaneously by French and Indian physicists in 1928. Attempts to account for the physical origin of the depolarised light in the spectrum had been made by French, Indian, and Soviet physicists, but the explanations proposed up to 1934 had been incorrect and will not be discussed here (see Ref. [11] and the literature cited there).

The origin of the Rayleigh line wing is explained correctly by Landau and Plachek in a paper dealing with a completely different topic [130]. In this paper the Rayleigh line wing is referred to only once as follows: "in the case of liquids the Debye relaxation time creates a definite role in the structure of this part".

This first indication of the relaxation origin of the Rayleigh line wing has played its role and has been significant.

The first quantitative relaxation theory of the spectrum of light scattered in a viscous liquid, based on the Maxwellian theory of viscosity, was proposed by Leontovich [131].

This simplified, but still quite complex theory, yields expressions describing the distribution of the intensity in the MB components due to the longitudinal and transverse thermal waves, as well as the distribution of the intensity in the Rayleigh line wing. Leontovich's calculations also give the degree of depolarisation of the scattered light as a function of the frequency [131].

One of the simplifications in Leontovich's theory is that it postulates the existence of just one anisotropy relaxation time τ. There are also other simplifications in this theory, but they will not be discussed, because use will be made of the results of more general theories. It should, however, be pointed out that the advantage of Leontovich's theory is its physical clarity in the description of the nature of the phenomenon and a demonstration of how this phenomenon is linked to other physical effects.

Leontovich's expressions for the distribution of the intensity in the Rayleigh line wing in the case of excitation of the scattering by natural light are as follows:

$$I_{\mathrm{V}}(\omega) = \frac{7A^2kT}{12\mu}\,\frac{2\tau}{1+\omega^2\tau^2}\,, \tag{70b}$$

$$I_{\mathrm{H}}(\omega) = \frac{A^2kT}{2\mu}\,\frac{2\tau}{1+\omega^2\tau^2}\,, \tag{70c}$$

where $I_{\mathrm{V}}(\omega)$ and $I_{\mathrm{H}}(\omega)$ are the intensities of the scattered light (considered as a function of the frequency measured from the frequency of the exciting light) with the vertical and horizontal polarisations, respectively; A is a quantity related to the Maxwellian constant M by $M = A\tau$; μ is the shear modulus. It follows from Eqns (70b) and (70c) that the depolarisation coefficient is $\rho = I_{\mathrm{H}}/I_{\mathrm{V}} = 6/7$, in agreement with the value given above.

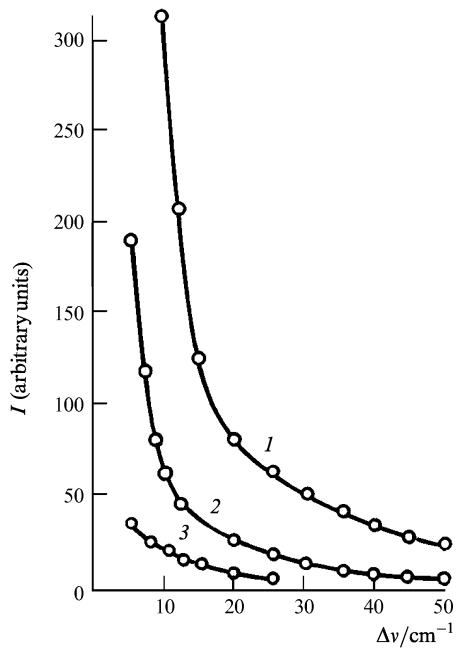

Figure 17. Distribution of the intensity in the far-frequency part of the Rayleigh line wing obtained for the scattering in salol at various temperatures (*1*) 120 °C; (*2*) 20 °C; (*3*) 0 °C [63].

Fig. 17 shows the distribution of the intensity in the far part of the Rayleigh line wing (RLW) of salol obtained at three different temperatures [63].

The theoretical expressions (70) provide rational ways of comparing theory with experiment. One such way, which I proposed [132], is as follows.

The reciprocal of the intensity $I(\omega)^{-1}$ is plotted along the ordinate and ω^2 along the abscissa [Eqns (70a)–(70c)]. Then the equation for the straight line can be written as follows:

$$I(\omega)^{-1} = c^{-1} + \frac{\omega^2\tau^2}{c}\,.$$

This straight line readily yields

$$\tau = \left\{\frac{\mathrm{d}[I^{-1}(\omega)]}{\mathrm{d}\omega^2}\right\}^{1/2}\,. \tag{71}$$

It is therefore possible to determine the relaxation time of the anisotropy fluctuations easily if the simplified theory is not in conflict with the experimental results. Fig. 18 shows schematically the results usually obtained experimentally for the RLW of various liquids in a wide frequency range.

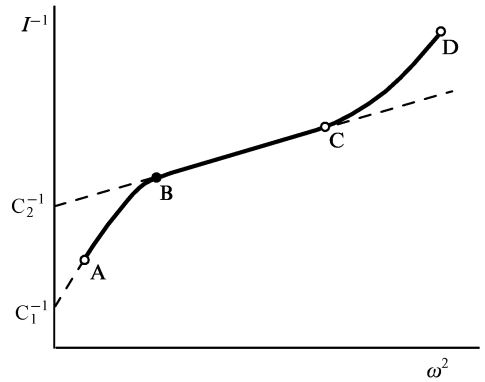

Figure 18. Schematic dependence of $I^{-1}(\omega)$ on ω^2 in the Rayleigh line wing in typical cases. Explanations in text.

This typical graph shows immediately that there are two regions with a linear dependence: AB and BC. It follows from this experimental result that the RLW has at least two anisotropy relaxation times: τ_1 (corresponding to AB) and τ_2 (BC), where $\tau_1 > \tau_2$. The region CD cannot be described by a straight line and very different explanations of this region have been put forward.

Fisher [133] assumes, like many others, that this far part of the RLW is described by an exponential frequency dependence of the intensity. Starunov [134] and others assume that the region CD can be described by a power function. The question cannot be regarded as finally resolved, because no reliable experimental investigations of this part of the spectrum have yet been made. In the region CD the intensity is very low and, therefore, within the limits of the considerable error of such measurements, both points of view can be 'confirmed'.

The anisotropy relaxation times for the regions AB and BC can be determined quite reliably by the above method, as reported in [132].

It should be stressed once again that the anisotropy relaxation times are determined along the spectrum on the assumption that only one physical process, which is the anisotropy relaxation, is responsible for the RLW. However, in general, there may be other processes that contribute to the spectrum of the depolarised light scattered in liquids.

Determination of the anisotropy relaxation time from the spectral line width is an indirect method and there have been so far no direct measurements which would have raised doubts about the values of τ_1 and τ_2 obtained from the spectrum of depolarised scattered light. Many such doubts have been raised and the results obtained have even been rejected outright, but there is no need to consider them here because the direct methods for the determination of τ, which became available a quarter of a century ago, are in surprisingly accurate agreement with the values found from the spectrum of depolarised light scattered in liquids. The optical methods for the direct determination of the anisotropy relaxation times began with the work of Duguay and Hansen [135] and are now conducted on a huge scale. Reviews of this topic were written a long time ago [136] and books on the subject are available (see, for example, Ref. [137]). The optical methods for the direct determination of the anisotropy relaxation time are in most cases based on the optical Kerr effect, observed for the first time by Mayer and Gires [138] and also by Maker, Terhune, and Savage [139], and can be described as follows: a short intense light pulse induces birefringence in a liquid of anisotropic molecules, in a manner similar to that induced by a static electric field (Kerr effect). The optical Kerr effect can therefore be used to construct an optical light switch which acts throughout an intense light pulse.

The use of intense picosecond light pulses has made it possible to determine directly the anisotropy relaxation time, called τ_1 above, determined from the region AB of the spectrum (Fig. 18). Relatively recently it had become possible to measure τ_2 with the aid of femtosecond light pulses, but the measurements are limited so far to several liquids listed in Table 1. The results given in this table are taken from reviews and original papers [137–142]. The direct and indirect measurements of τ_1 are in good agreement. There is also a good agreement for τ_2 in the case of carbon disulfide studied on different occasions, but a strong divergence between the results of the direct and indirect measurements of τ_2 of nitrobenzene [134, 136, 137], and those obtained with femtosecond pulses [142]. Further work will show whether this is a physical process or the difference which results from imperfections of the measurements.

Table 1. Room-temperature anisotropy relaxation times τ_1 and τ_2, determined indirectly and directly.

Liquid	Deduced from spectra		Direct measurements	
	$10^{12}\tau_1$/s	$10^{12}\tau_2$/s	$10^{12}\tau_1$/s	$10^{12}\tau_2$/s
Carbon disulfide	2.4	0.21	$2+0.5$	0.24
Nitrobenzene	44.6–39	3.6; 1	47.4	31.8 ± 2.0
Toluene	4.1	0.17	5 ± 1	—
Benzene	3.3	0.24	4 ± 0.5	—
Chlorobenzene				6.3 ± 0.3

The good agreement between the direct and indirect measurements of τ_1 makes it possible to use the spectrum of depolarised light scattered in various media to study relaxation processes and to find τ_1. Development of femtosecond pulse methods should perform a similar task in the case of τ_2.

Fast processes can be studied by optical switches right down to times τ_1 governing the response time of such switches.

Ordinary organic liquids can be used in the range of times defined by τ_1 and τ_2. The best liquid for short times is carbon disulfide for which the permissible time interval lies between 2.4×10^{-12} and 2×10^{-13} s. The response of a femtosecond pulse in the region CD (Fig. 18) is not yet clear because the physical origin of this spectrum has not yet been identified. For pulses longer than 10^{-12} s this is a relatively simple task, namely one should select such liquids as nitrobenzene ($\tau_1\approx5\times10^{-11}$ s) or even more viscous media for which τ_1 can be $\sim10^{-6}-10^{-5}$ s.

Selection of the optical switch material for times shorter than 10^{-13} s is more difficult, but still can be done. In the latter case one needs to rely on the electronic relaxation times of the switch, $\sim10^{-15}$ s, and these are the times expected for glasses and some other materials in which the Kerr (Voigt) effect is governed by the electronic polarisation but not by the orientational effect.

A natural and important question arises as to the microscopic nature of the various parts of the RLW shown schematically in Fig. 18.

Since the whole spectrum of depolarised light scattered in various media is under intensive investigation, new contributions will be made to the understanding of the nature of the wing, but at this stage the most satisfactory and physically clear is the explanation proposed by Starunov [134], which can be described briefly as follows.

Any anisotropic molecule in a liquid is in a potential well created by the environment of its neighbouring molecules. This molecule in a potential well exhibits at least two types of thermal motion, one of which is due to rotational diffusion with jumps to other potential wells. Such motion of anisotropic molecules is relatively slow and modulates the scattered light which contributes to the region AB (Fig. 18). The relaxation time τ_1 determines the rotational diffusion time.

In the interval between two diffusion rotations the molecule in a potential well executes, under the influence of thermal effects, librations (vibrations in a potential well), which lead to 'fast' modulation of the scattered light and make their own contribution to the region BC in the spectrum (Fig. 18), so that τ_2 is a characteristic ('period') of the librational motion.

The scattering in liquids is not on single molecules, but on anisotropy fluctuations, so that τ_1 and τ_2 should be regarded as the effective measures of the processes described here.

5.3 Further investigations of the spectrum of light scattered on anisotropy fluctuations. Detection of the doublet structure of the spectrum

Experimental investigations of the frequency distribution of the intensity of light scattered on the anisotropy fluctuations, carried out with the aid of spectroscopic apparatus

with low resolution and with excitation sources that have wide spectral lines, have provided only a general picture of the phenomenon.

It would be pointless to use such instruments as the Fabry–Perot interferometer to study the RLW of liquids such as benzene, toluene, and many others with short relaxation times τ_1 and τ_2 and, consequently, wider spectral regions.

In the case of liquids with a narrow region AB (Fig. 18) a Fabry–Perot interferometer could be used to find τ_1 and its dependence on the viscosity (temperature).

I used a Fabry–Perot interferometer with the dispersion (free spectral) range $\Delta\nu \sim 1\,\mathrm{cm}^{-1}$ in investigations of this kind [63, 137a] to observe clearly the MB scattering components. The excitation was provided by a wide line at 4358 A from the spectrum of mercury emitted in a gas discharge and its scattered-light spectrum was recorded with a photographic plate. At that time our laboratory did not have access to apparatus needed in the photoelectric method.

In this investigation the scattered light was observed at the scattering image of 90° to the direction of the exciting light, passed through a Wollaston prism, and was split into two beams with mutually perpendicular polarisations: normal to the scattering plane I_V and parallel to the scattering plane I_H. The light then passed through a $\lambda/4$ plate which made the polarisation circular and ensured identical conditions for the propagation of both beams through a monochromator selecting $\lambda = 4358$ A, a Fabry–Perot interferometer, and objectives. A photographic plate was used to record the scattered-light spectrum in these two polarisations. In one half of the plate various interference orders were recorded for light containing the MB components, which included the central component in the superimposed narrow (AB in Fig. 18) part of the wing, whereas the other part of the plate recorded only the light from the I_H spectrum, when only the narrow part of the RLW could be seen. The wide part of the wing, which considerably exceeded the dispersion range $\Delta\nu$, the region BC, and the rest of the wing were all superimposed in various orders and formed the background [10, 11, 137a]. In the case of benzene, toluene, etc. there was a continuous background to I_H and in the case of I_V a MB component was observed against the continuous background. The spectra of light scattered in quinoline, salol, benzophenone, etc. were quite different [10, 11, 137a]. In the case of these liquids the spectrum of I_H had a weak background and a very strong line, whose width was of the order of the spectral width of the exciting light. For I_V there was also a strong line lying within the MB doublet. This strong line was due to the region AB (Fig. 18) of the RLW.

The anisotropy relaxation time of such liquids, found from the region AB (Fig. 18), would be one or even two orders of magnitude longer than τ_2 found from the region BC.

According to the initial relaxation theory of the spectrum of light scattered on anisotropy fluctuations, proposed by Leontovich [131], the anisotropy relaxation time is proportional to the shear viscosity and inversely proportional to the absolute temperature T:

$$\tau = V\frac{\eta}{kT}\,, \tag{72}$$

where V is a constant (according to Leontovich, it is the volume of a molecule) and k is the Boltzmann constant.

The first experimental determinations of τ and of its temperature dependence have shown that there is a qualitative agreement with Eqn (72), but — for example in the case of salol — there is no quantitative agreement. Between 20 and 170 °C the shear viscosity varies by a factor of 80 and τ calculated from Eqn (72) varies by a factor of 120, whereas the experiments show that in this temperature range τ changes by a factor of just ~ 4.

In calculation of τ from Eqn (72) it is hardly valid to substitute the shear viscosity η measured in a static experiment, as is usually done, because the formation of the RLW is related to high frequencies at which the shear viscosity may change considerably because of relaxation.

Further experimental investigations of the RLW have been hindered by the considerable width of the exciting line from the mercury spectrum generated in high-pressure lamps. The width of the exciting line is greater than the width of the emitted (scattered) line.

Investigations of the RLW have been continuing. The reviews of the results obtained can be found in Ref. [11] and in the book by Vuks [144], but new data have been obtained only when satisfactory light sources have been used, such as the mercury lamp with the ^{198}H isotope [82]. In our laboratory we made a lamp with cadmium vapour emitting a strong and narrow line at $\lambda = 6438$ A, intended for detailed investigations of the spectra of the molecular scattering light in general [145].

However, such investigations have not been carried out. The traditional light sources have been replaced with lasers emitting intense lines with a degree of monochromaticity that could not have been even dreamt of by the experimentalists. The situation in the case of the narrow part of the RLW has also changed drastically.

Our first interferometric experimental investigations with a laser [22], which immediately gave new results on the width of the MB component, have revealed a very narrow part of the RLW of liquid nitrobenzene [146].

A more detailed experimental study of this part of the wing in nitrobenzene and quinoline has made it possible to observe a new effect in the spectrum of depolarised light scattered in these liquids. In our first paper on this topic [147] we stated right at the beginning: "the spectrum of thermal dipolarised scattering of light (Rayleigh line wing) revealed a new phenomenon in which the x component, $I_{VH}(\omega)$, in this spectrum is split into two. The separation between the components of this doublet is considerably less than the separation between the MB components."

Our first explanation of this new phenomenon was as follows: light scattered by the anisotropy fluctuations caused by shear strains is modulated by the Fourier component of these strains or, in other words, by strongly damped transverse acoustic waves.

In our first experiments the detector was a photographic plate. We subsequently acquired electronic means for recording the spectra. Fig. 19 shows a record of the fine structure of the RLW in salol [148] and Fig. 20 gives the spectra of the molecular scattering of light in liquid aniline, recorded for different polarisations of the scattered light and showing all the singularities reported previously [143, 149, 150]. Here, I_{VV} represents the MB components, I_{VH} is the fine structure of the Rayleigh

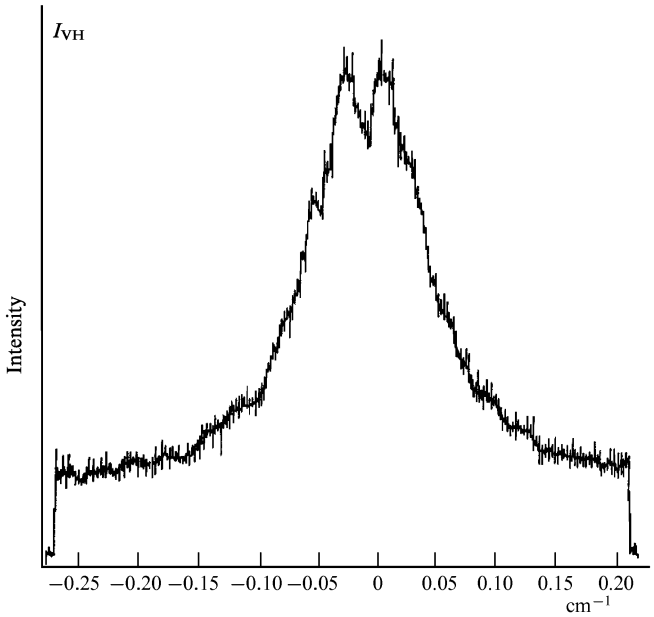

Figure 19. Fine structure (doublet) of the Rayleigh line wing of salol at 76.7 °C [148].

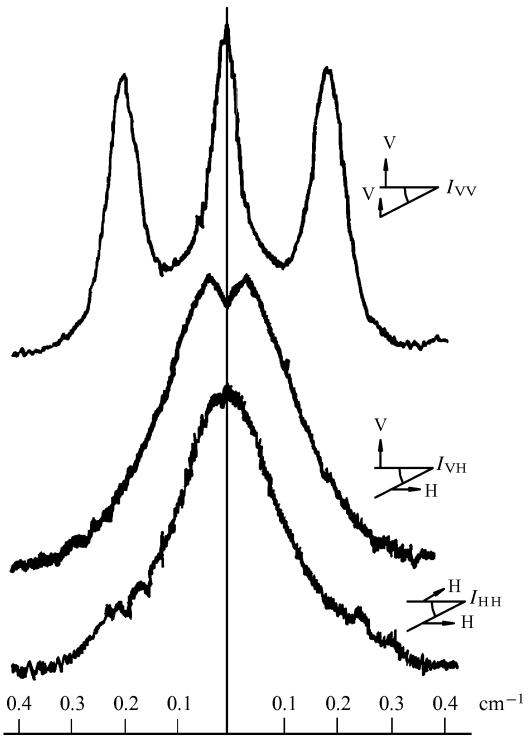

Figure 20. Spectrum of the molecular scattering of light in aniline, obtained for various polarisations. Explanations in text [149].

line wing, and finally I_{HH} shows some singularity at the frequency of the MB component associated with the interaction between the longitudinal acoustic modes and the orientational motion in liquids [151].

The observed doublet structure of the wing had been unexpected and even gave rise to a misunderstanding primarily because the presence of a structure (two broad lines) in the RLW should mean that the scattered light is modulated by a process with nonmonotonic time dependence. This process can be the propagation of strongly damped transverse sound, as mentioned above. However, since the doublet structure of the RLW is observed in liquids with viscosities in the range 2–4 cP, it is clear that the hypothesis of the propagation of transverse sound is in conflict with classical hydrodynamics, which predicts that at the acoustic wavelength Λ the absorption coefficient α of transverse sound in such a medium is 2π and, consequently, such sound cannot propagate. According to hydrodynamics, such a medium can support only a Newtonian 'viscous wave' or, in other words, exponentially decaying sound for which the argument of the exponential function $\alpha\Lambda$ is 2π [14, 152–154]. Such a modulating function cannot give rise to a doublet in the spectrum and can only alter the width of the spectral band or line.

The name 'viscous wave' is quite arbitrary because the amplitude of such a 'wave' decreases by a factor of 535 in one wavelength and one cannot speak of wave-like motion.

However, continuation of the experimental investigations has definitely confirmed the existence of a doublet as an essentially new unusual phenomenon.

Over a year after our first paper [147], Stegeman and Stoicheff [151] confirmed our observations and explanation of the nature of the phenomenon in the case of nitrobenzene, quinoline, aniline, and *m*-nitrotoluene.

This new phenomenon has attracted the interest of experimentalists and theoreticians working in a number of laboratories and countries. We shall give only some of the results of the experimental investigations of the fine structure of the RLW for liquids consisting of anisotropic molecules with viscosities that are in approximately the same range.

Fig. 21 shows the fine structure of quinoline as a function of the scattering angle θ [207] and we can see that the pronounced doublet disappears at high scattering angles.

The fine structure of the wing has also been studied in benzyl alcohol [171] and in α-bromonaphthalene [170]. Fig. 22 shows the fine structure of the RLW of triphenyl phosphate at 70.2 °C for the scattering angle of $\theta = 90°$ and $\lambda = 5145$ A: the fine structure disappears at 41.6 °C and $\theta = 90°$ [156].

The temperature dependence of the fine structure has also been revealed clearly by an experimental study in the

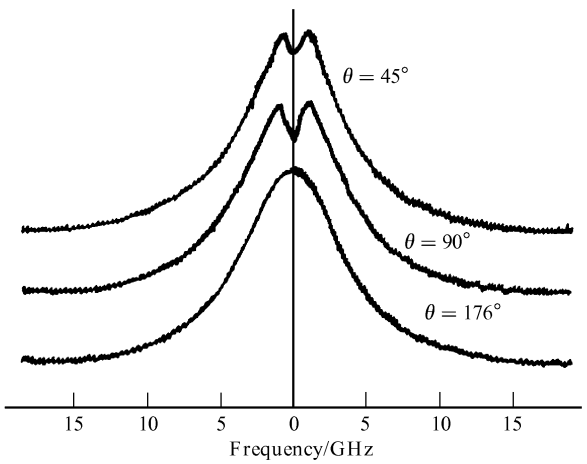

Figure 21. Fine structure of the Rayleigh line wing in quinoline for various scattering angles from $\theta = 45°$ to $\theta = 176°$ [207].

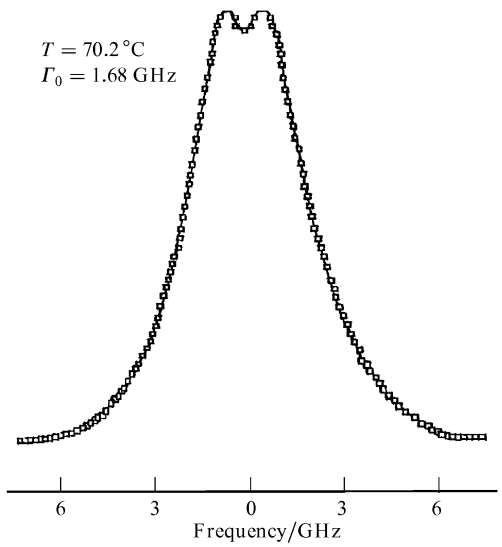

Figure 22. Fine structure of the Rayleigh line wing of triphenyl phosphate at 70.2 °C [156].

specific case of anisaldehyde [157] between 79 and 6 °C (Fig. 23). If the fine structure does indeed appear as a result of modulation of the scattered light by a damped acoustic wave and if such modulation can be detected at 79 °C, it would seem that it should be even more readily visible at the lower temperature of 6 °C, whereas the experimental evidence shows that the reverse is true. This result is in conflict with hydrodynamics and cannot be reconciled in any way with the Maxwellian scheme of viscosity.

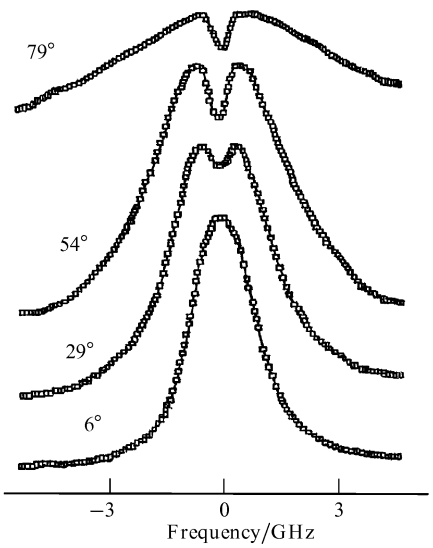

Figure 23. Temperature dependence of the fine structure of the Rayleigh line wing of anisaldehyde obtained in the temperature interval from 79 to 6 °C [157].

A clear fine structure of the RLW has also been observed for acetophenone at 15 °C (Fig. 24) [158], in salol at 81 °C (curve *1* in Fig. 26) [148], and in many other cases. There is no space to give all the evidence and there is no need for this.

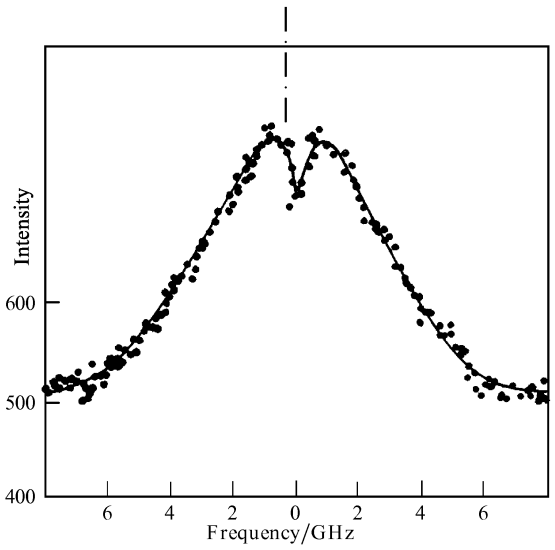

Figure 24. Fine structure of the Rayleigh line wing of acetophenone [158].

In the case of a substance such as carbon disulfide, consisting of anisotropic molecules, there is no fine structure at room temperature and the intensity falls monotonically on either side of the maximum located at the unshifted frequency.

Enright and Stoicheff [159] carried out a careful and detailed investigation of the RLW for $I_{VH}(\omega)$ at nine different temperatures between 162 and 192 K, and did the same for $I_{HH}(\omega)$ at six different temperatures.

In the case of $I_{VH}(\omega)$ the fine structure became less clear as the width of the depolarised spectrum increased. Fig. 25 shows the spectrum of CS_2 obtained at two different temperatures at which the fine structure could be observed.

This result is very important because it shows that a liquid consisting of anisotropic molecules can be in a state in which its viscosity lies within an interval of $\sim (1-2) \times 10^{-2}$ P, when this scattered-light spectrum exhibits the fine structure of the RLW. This is evidence that the

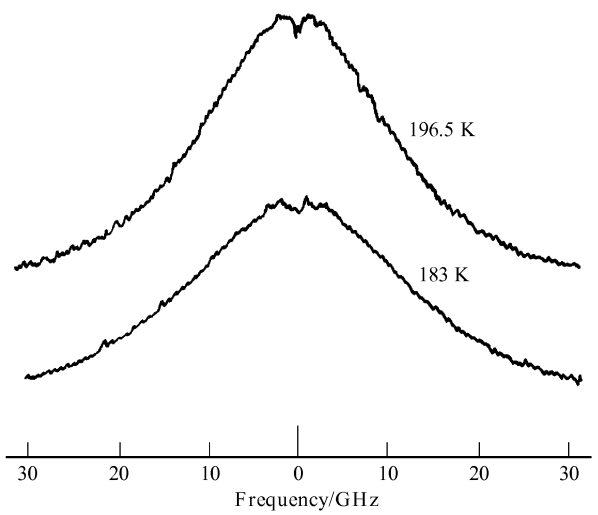

Figure 25. Fine structure of the Rayleigh line wing of CS_2 at two temperatures [159].

observed fine structure is of general nature. Enright and Stoicheff assume, with good grounds, that the fine structure may also be observed in such simple liquids as nitrogen and oxygen.

At the beginning of the experimental investigations the very first observation of the fine structure of the RLW provided the correct but purely qualitative explanation of the physical nature of the observed effect [147, 160, 165]. A quantitative description of this fine structure is now needed. It is not permissible to calculate the anisotropy fluctuations in the same way as in the case of the density, entropy, and concentration fluctuations because the anisotropy is not a thermodynamic parameter but an internal one. The anisotropy fluctuations and the spectrum of light scattered on such fluctuations have to be calculated by a completely different procedure.

The first quantitative, simplified, but still very complex calculation of the spectrum of the light scattered on the anisotropy and pressure fluctuations was published by Leontovich [131], as mentioned above. He obtained formulas for $I(\omega)$ in the region near the exciting line [131].

We shall not repeat the whole complex procedure of obtaining the results in question (they can be found in Ref. [131] or in Ref. [11]). The final result will be given. If the vector $\boldsymbol{E}$ of the incident linearly polarised light lies in a plane perpendicular to the scattering plane, then

$$I_{\mathrm{VH}}(\omega) = \frac{A^2}{8\mu}\left[\frac{2\omega^2\tau\cos^2(\theta/2)}{\omega^2+\tau^2(\omega^2-\Omega_{\mathrm{T}}^2)^2}+\frac{2\tau\sin^2(\theta/2)}{1+\omega^2\tau^2}\right] . \quad (73)$$

If the same vector $\boldsymbol{E}$ lies in the scattering plane, then

$$I_{\mathrm{HH},\theta=90}(\omega) = \frac{A^2}{8\mu}\left[\frac{3(\omega^2-\Omega_{\mathrm{L}}^2)^2\tau}{(\omega^2-\Omega_{\mathrm{L}}^2)^2+\omega^2\tau^2(\omega^2-\Omega_{\mathrm{S}}^2)^2} + \frac{2\tau}{1+\omega^2\tau^2}\right] . \quad (73')$$

Here, $\Omega_{\mathrm{L}} = 2qv_{\mathrm{L}}$, $\Omega_{\mathrm{T}} = 2qv_{\mathrm{T}}$, $\Omega_{\mathrm{S}}^2 = \Omega_{\mathrm{L}}^2 + (4\Omega_{\mathrm{T}}^2/3)$, $A = M/\tau$, where M is the Maxwellian constant, μ is the shear modulus, and the frequency ω is measured from the frequency of the exciting light $v_{\mathrm{L}} = \sqrt{1/\beta_S}\rho$, β_S is the adiabatic compressibility, and $v_{\mathrm{T}} = (\mu\rho)^{1/2}$. The Maxwellian scheme yields the following relationship between the viscosity and elasticity:

$$\eta = \mu\tau_{\mathrm{M}} . \quad (74)$$

There are two terms in Eqn (73): the first represents the discrete components at frequencies $\pm\Omega_{\mathrm{T}}$ and the second is superimposed on the shifted components and has its maximum at the unshifted frequency ($\omega = 0$). Under certain conditions (at a specific temperature) the predicted profile can resemble the doublet structure presented in Figs 19–25.

This is the reason why we assumed [147, 160–162] that the doublet structure observed by us in the near part of the wing can be explained by Leontovich's theory [131] and expression (73) which follows from it. This opinion was shared by other physicists [163, 170]. The same misunderstanding can also be found in a book by Berne and Pecora [172].

This interpretation of the experimental results can be confirmed or rejected by further experiments and, in particular, by determination of the temperature dependence of the doublet components.

According to Leontovich's formula (73) cooling and an increase in the shear viscosity (when the relaxation process 'converts' the viscosity into elasticity) should increase the hf shear modulus μ, velocity of sound v_{T}, and, therefore, Ω_{T}. Consequently, an increase in the viscosity should increase the separation between the doublet maxima and finally at very high viscosities and in glasses there should be a clear triple with two narrow shifted components and the central one. This spectrum should superficially resemble the spectrum of light scattered by the pressure and entropy fluctuations, but the origin of this spectrum is completely different and represents depolarised light. These are the predictions that follow from Leontovich's formula (73) [131].

However, the first experimental results obtained in our studies [165–169] produced nothing like this and the subsequent experiments simply confirmed the earlier results.

In an experimental study of the temperature dependence of the frequency positions of the maxima of the doublet components of the doublet observed in the RLW [147] it is necessary to select a liquid which consists of molecules as anisotropic as possible and with a shear viscosity which can be varied between the widest possible limits by altering the temperature of the liquid. On the basis of my previous experience, I selected salol for this purpose [164]. It shows clearly the doublet structure of the Rayleigh wing and its viscosity (after suitable purification) can vary from very low values to that of the glassy state [165, 168].

If the separation between the maxima of the doublet components (lines) is denoted by $2\Delta\nu_{\max}$, cooling (increase in the viscosity) should make it possible to follow the changes in $2\Delta\nu_{\max}$. Where Leontovich's theory [131] predicts an increase in $2\Delta\nu_{\max}$ when the viscosity rises, our experiments gave a directly opposite result. An increase in the viscosity reduced somewhat $2\Delta\nu_{\max}$ [165]. The same effect was reported by Stegeman [163]. This was an unexpected and surprising result. Even more surprising was the behaviour of the investigated spectrum at still lower temperatures. Between 120 and 46 °C a doublet was observed, but at +45 °C the doublet structure disappeared and there was no RLW structure of salol between −2 and +45 °C: the profile was a smooth dome.

This behaviour of the spectrum was not predicted by Leontovich's theory [131] or by any other theory available at the time.

In our experiments we continued to observe the spectrum when temperature was reduced even further in a continuous manner. At −2.5 °C a nonmonotonic dependence appeared on the sides of the smooth dome and then clear lines appeared; the value of $2\Delta\nu_{\max}$ increased as the viscosity became higher and finally a clear triplet was observed. The appearance of the side components exactly followed the behaviour predicted by Leontovich's theory [131], at least in the qualitative sense.

Fig. 26 (curves *3* and *4*) shows how the theoretically predicted and the experimentally observed triplet behaves in the case of the spectrum of light scattered in salol at −20 °C [148]. The narrow shifted components are evidence of weak damping of a transverse acoustic wave in salol at −20 °C and the narrow central line indicates that the anisotropy relaxation time τ is long compared with the value of τ at a temperature which is higher, but still such that a triplet is observed [148].

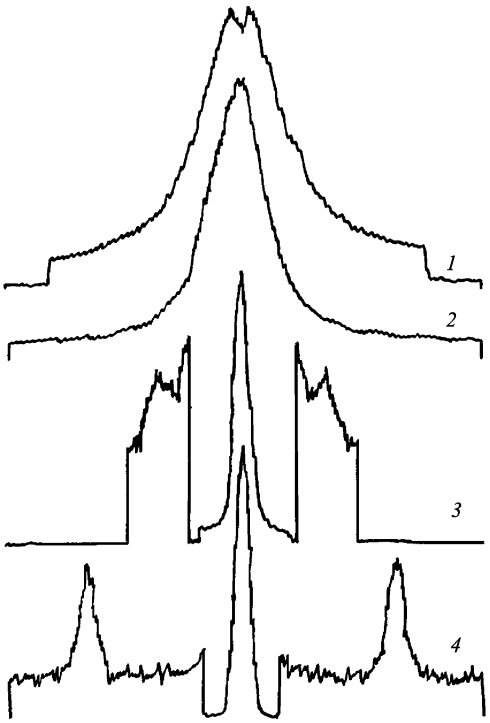

Figure 26. Dependences $I_{VH}(\omega)$ obtained for salol at various temperatures (for various viscosities): (*1*) 81 °C; (*2*) 36 °C; (*3*) 15 °C; (*4*) 20 °C [148].

The spectrum of depolarised light had also been studied for the scattering in benzophenone $[(C_6H_5)_2CO]$ and this was done in a wide range of the shear viscosity. It was found that the changes in the spectrum with temperature were exactly the same as in the case of salol.

Initially, between 115 and 15 °C, the fine structure of the RLW was clearly visible, but between +15 and −2.5 °C it was no longer detectable. Beginning from −2.5 °C a triplet appeared and remained clear down to −55 °C, exactly as described earlier for the case of salol.

In these experiments on benzophenone the shear viscosity varied by 12 orders of magnitude from 10^{-3} to 10^9 P [168].

When the experimental results are replotted graphically so that the ordinate gives $2\Delta\nu_{max}$ and the abscissa represents temperature, the results are as shown in Fig. 27 for salol (a) and benzophenone (b). We can see clearly two branches of each spectrum which are practically identical for both substances.

At higher temperatures the points correspond to the value of $2\Delta\nu_{max}$ for the doublet spectrum and quite arbitrarily this is called the 'high -temperature' branch, whereas the points lying at lower temperatures represent $2\Delta\nu_{max}$ corresponding to the positions of the displaced components in the triplet spectrum and are called the 'low-temperature' branch.

The continuous curves represent the optimal representation of the experimental points.

One further nontrivial observation in the spectrum of molecular scattering of light should be mentioned: it was first reported by Stegeman and Stoicheff [151, 163].

This observation related to $I_{HH}(\omega)$. Fig. 28 shows its nonmonotonic behaviour in the range of frequencies corresponding to the superposition of the MB components. A more detailed experimental investigation of this region showed that, in accordance with the predictions of Leontovich's theory — Eqn (74) in Ref. [131], the longitudinal acoustic and orientational motion modes interact: the curve is similar to the anomalous dispersion curve in Fig. 28.

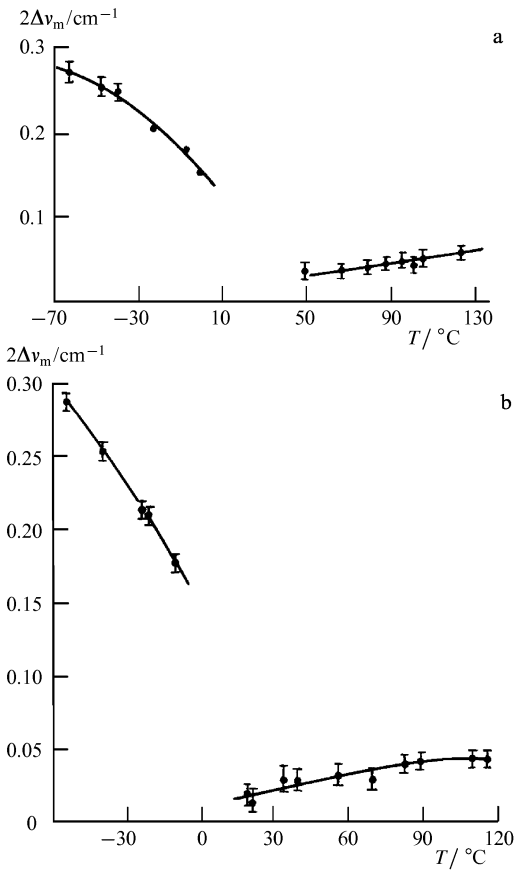

Figure 27. Temperature dependences of the positions of the maxima ($2\Delta\nu_{max}$) of a doublet and triplet in the spectrum of light scattered in salol (a) and benzophenone (b) [165, 166, 168].

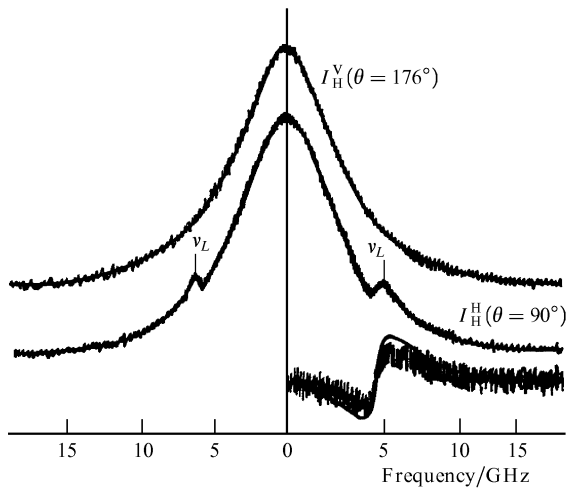

Figure 28. Spectra of quinoline obtained for the $I_{HH}(\omega)$ polarisation and $\theta = 90°$. The effect of the interaction between the acoustic and orientational modes of motion is observed in the region of the MB scattering components [151b, 163].

This is the experimental behaviour of the spectrum of molecular scattering of light by the anisotropy fluctuations, specifically the behaviour of the RLW, and these are the qualitative and simplified explanations of this behaviour.

6. Quantitative description of the molecular light-scattering spectra

The history of how the theory providing a quantitative description of the molecular light-scattering spectra has reached the present high level of development is interesting and even fascinating, like the history of the problem as a whole.

I shall consider only one specific topic to demonstrate how fascinating it is [173]. A study of the history of the subject as a whole is a task for the future. However, I hope that this will be done.

At this stage I would like to make just a few comments how the quantitative theories have appeared.

Most probably the first laboratory observations of the scattering of light were those made by Tyndall in 1869 (see Ref. [11]). He observed the scattering of arc light by small solid particles and detected 'blueing' of the scattered light. Evidently this experiment provided the stimulus that led Lord Rayleigh to develop a quantitative theory of the scattering by particles (such as dust) smaller than the wavelength of light. In 1890 Rayleigh derived a formula which is still valid. It follows from the Rayleigh formula that the intensity of the scattered light is proportional to the sixth power of the particle radius (r^6) and inversely proportional to the fourth power of the wavelength of light (λ^{-4}). This is quite sufficient to account for the sky being blue. However, it was soon found that the absence of dust in the atmosphere (in high mountains) produces an even more strongly saturated blue sky than in the presence of much dust. Rayleigh then concluded that the gas molecules forming the atmosphere themselves scatter light and thus developed a theory of the scattering of light by isolated molecules (1900).

In his theory the scattered-light intensity is inversely proportional to the fourth power of the wavelength of the incident light: $I \propto \lambda^{-4}$. This is the Rayleigh law and it accounts for the blue colour of the sky. Rayleigh's theory of the scattering of light in the atmosphere led to controversy (see Mandelstam [6], Vol. 1), but this point will not be discussed here.

This fundamental work of Rayleigh provides a basic understanding of the phenomena in atmospheric optics.

Various theories of the critical opalescence are continuing to be discussed and new ones are being proposed [98–100]. This opalescence appears in a critical liquid–vapour region or in solutions which undergo phase separation. Initially the enormous intensity of the scattered light, which appears in a narrow temperature interval (critical range), had not been explained correctly. Finally, Smoluchovsky [2] provided a correct explanation of the opalescence in 1908: he attributed it to a strong rise of the density or concentration fluctuations in solutions. This fruitful idea of fluctuations is the basis of the Einstein theory of scattered light. Einstein [3] derived a fundamental formula for the integral intensity of light scattered in liquids and solutions (1910). Mandelstam [4] also used the idea of fluctuations to calculate the scattering by the surface of a liquid and observed this effect (1913); this work was continued by the development of a general theory by Leontovich [46].

For a long time the fluctuation theories have been based on thermodynamics, which does not include such concepts as frequency and dispersion. These thermodynamic theories have included those in which the intensity of light scattered by adiabatic and isobaric fluctuations is calculated [11]. The relationship between the intensities resulting from the scattering by the two types of fluctuations has been obtained and it is known as the Landau–Placzek (Plachek) theory [11, 130], but a theory covering the whole spectrum of the molecular scattering of light has not been developed.

In the twenties in the countries where the studies of light scattering have been pursued particularly actively the experimentalists have been preoccupied with the search for the optical analogue of the Compton effect (in India), with modulation of scattered light by elastic thermal (Debye) waves (Russia), and with what is now known as the combination scattering of light or the Raman effect (France).

In 1928 the combination scattering of light was discovered simultaneously in India and Russia. Moreover, the wing of the Rayleigh line was observed practically simultaneously in France and India [191, 192]. These discoveries have stimulated theoretical investigations, but they have been focused mainly on the combination scattering of light in solids and are only partly applicable to the subject of my review [174–178].

In the late thirties I was experimentally investigating the Rayleigh line wing (RLW) of various liquids and this wing was also being investigated by Gross and Vuks [144]. M A Leontovich was working on a spectral theory of the molecular scattering of light. He developed his theory [131] and derived expressions for the frequency distribution of the intensity of light scattered as a result of fluctuations of the anisotropy and pressure. The scattering of light due to the entropy fluctuations was ignored by Leontovich not because he could not deal with this type of scattering, but because the theory had already proved too complex and serious simplifications were needed. However, Leontovich put forward the first quantitative phenomenological theory of the spectrum of the molecular scattering of light. He managed to do this and to publish the theory before Germany invaded the Soviet Union. It appeared in 1941. My experimental results were also ready, but war intervened before they were published and this was done only in 1945 [132]. They were analysed and discussed on the basis of Leontovich's formula [131].

The last war began in Russia in 1941 and even earlier in France and England and other countries. Naturally, at that time the physicists were not preoccupied with the spectral theories of light scattered in condensed media. The papers on scattered-light spectroscopy began to appear only in the fifties and soon the dispersion of the velocity of sound was discovered on the basis of the MB spectra [10, 11, 20, 21]: the results demonstrated that the thermo-dynamic theories of the scattering of light are unsatisfactory and that it is necessary to allow for the frequency dependences of thermal, mechanical, and internal parameters of the medium, which — as mentioned above — is impossible on the basis of classical thermodynamics.

It has also been found that a nonthermodynamic derivation of the formula for the intensity of light scattered

due to the adiabatic fluctuations of the density can modify somewhat the Landau – Placzek relationship [130] and that this improves the agreement between theory and experiment [11, 201].

The fifties saw accumulation of fairly substantial data which needed the development of a general theory that took into account the various processes of the dispersion and interaction of the modes of different types of motion in a condensed medium. The development of such a phenomenological theory of the spectrum of light scattered because of various fluctuations (including the anisotropy fluctuations) was undertaken, following Leontovich [131], by Rytov on the basis of his correlation theory of thermal fluctuations in an isotropic medium [179]. He carried out fundamental work presented in two papers [180, 181], which include new predictions — for example, a compression wing which is a new part of the spectrum — which hitherto had not been observed experimentally. However, Rytov made a mistake [179 – 181], pointed out subsequently by Romanov, Solov'ev, and Filatova [182].

The problem was as follows: Rytov [179 – 181] used an 'incomplete description' in which the number of generalised coordinates does not include the internal relaxing parameters and the dispersion is taken into account formally by introduction of complex frequency-dependent elastic moduli, specific heats, and thermal expansion coefficients. Romanov et al. showed [182] that in the presence of internal relaxation processes this incomplete description can be used to find fluctuations of the generalised coordinates, but not of the generalised forces. Therefore, in Rytov's work [179 – 181], in which the fluctuation – dissipation theorem is used as the main working instrument, an incomplete description is not permissible. This was accepted by Rytov and he immediately developed a theory on the basis of a complete description [183, 184] free of the earlier shortcomings [179, 180].

Rytov's new theory appeared in 1970, forty years after the work reported in Refs [174] and [175]. The fundamental phenomenological theory [183] was followed by a number of theoretical investigations providing a phenomenological description of the spectrum of light scattered by various fluctuations [185 – 187]. In the time between the publication of Refs [179 – 184] and of Ref. [186], Mountain produced a series of papers [188 – 190] in which an account was taken of thermal relaxation with a single time constant τ and expressions were obtained for the distribution of the intensity in the central or Rayleigh line and in the MB components. The Landau – Placzek relationship was discussed in detail by Mountain. The spectra of light scattered on the anisotropy fluctuations were ignored. However, it can be said that by the seventies a quantitative phenomenological theory of the spectra of light scattered on fluctuations of various types had been developed and has proved to be capable of a satisfactory description of the experimental results.

By this time an experimental observation was reported of the fine structure of the RLW, as described above.

When the initial doubts about the reality of the observed fine structure had been resolved, a whole stream of theoretical investigations, explaining this fine structure, appeared.

7. Ratio of the integral intensities of light scattered on isobaric and adiabatic density fluctuations in a dispersive medium

In the spectrum of molecular light scattering the central (or Rayleigh) component I_c is due to the scattering by isobaric fluctuations and is described by Eqn (3). Both MB components $2I_B$ are due to adiabatic fluctuations and are given by Eqn (2). The ratio of these intensities is:

$$\frac{I_c}{2I_B} = \frac{I_{is}}{I_{ad}} = L\frac{\sigma^2 T}{\rho C_P \beta_S} , \tag{75a}$$

where

$$L = \left(\frac{1}{\sigma}\frac{\partial\varepsilon}{\partial T}\right)_P^2 \left[\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_S^2\right]^{-1} .$$

If the thermodynamic relationship described by Eqn (6) is taken into account and it is assumed that $L = 1$, the familiar Landau – Placzek formula [130] is obtained from Eqn (75a):

$$\frac{I_c}{2I_B} = \gamma - 1 . \tag{75b}$$

All the relationships given above are purely thermodynamic and apply to a dispersion-free medium. In reality, there are strictly speaking no such media and, therefore, the Landau – Placzek formula gives estimates of the quantities which are in quantitative disagreement with experiments.

The MB components are due to hf ($\sim 10^{10}$ Hz) thermal waves and, therefore, the dispersion must be taken into account in a quantitative description of the ratio $I_c/2I_B$.

This was precisely the calculation which I carried out [201] and which yielded a nonthermodynamic expression for I_{ad}. The quantity I_{is} is related to long wavelengths and, therefore, we can use Eqn (3) and retain the relationship (75a) bearing in mind that $\beta = [\rho v^2(\omega)]^{-1}$.

Therefore, expression (75a) allows partly for the dispersion via the dispersion of the velocity of sound. In view of this, the value of I_{ad} becomes smaller and Eqn (75a) better describes the experimental results. Nevertheless, a better agreement between theory and experiment still needs to be achieved.

The dispersion of the velocity of sound, which originates from relaxation of the bulk viscosity, reduces the value of I_{ad}, but — as demonstrated by Rytov [181] — such relaxation creates a new region of the spectrum of scattered light which is called the compression wing. This wing is superimposed on the central component and, consequently, if the experimental compression wing is sufficiently narrow, the value of $I_c/2I_B$ increases and approaches the experimental results. Therefore, the dispersion of a medium must result in some redistribution of the intensity in the scattered-light spectrum in such a way that the contribution subtracted from $2I_B$ is added to I_c.

In Mountain's theory of the distribution of the intensity in the spectrum of light scattered in a dispersive medium as a result of the density of fluctuations [189] the following expression describes the ratio of the intensity at any frequency:†

$$\left(\frac{I_c}{2I_B}\right)_\omega = L\frac{(\gamma - 1)/\gamma + \mathcal{A}/\mathcal{C}}{\mathcal{B}/\mathcal{C}} \tag{75c}$$

† The expression obtained in Ref. [189] is multiplied here by L Joules, so that the thermodynamic expression (75a) is obtained in the limit $\omega \to 0$.

where

$$\mathcal{A} = (v_\infty^2 - v_0^2)q^2 - \left(\frac{v_\omega}{v_0} - 1\right)\left[\frac{v_0^4}{v_\omega^4\tau^2} + v^2q^2\left(\frac{\gamma-1}{\gamma}\right)\right]$$

$$\mathcal{B} = \left[1 - \frac{v_0^2}{v_\omega^2}\left(\frac{\gamma}{\gamma-1}\right)\right]\left(v_\omega^2q^2 + \frac{v_0^2}{v_\omega^2\tau^2}\right) - (v_\infty^2 - v_0^2)q^2$$

$$\mathcal{C} = \frac{v_0^4}{v_\omega^4\tau^2} + v_\omega^2q^2$$

In the hf limit, $vq\tau \gg 1$, it is found from Eqn (75c) that

$$\left(\frac{I_c}{2I_B}\right)_{\tau\to\infty} = L(\gamma-1)\left(1 + \frac{\gamma}{\gamma-1}\right)\frac{v_\infty^2 - v_0^2}{v_0^2}\ , \qquad (75d)$$

and apart from the factor L, the formula (75d) is identical with that derived earlier by Rytov [181].

8. Quantitative theory of the spectrum of light scattered in an isotropic medium consisting of anisotropic molecules

At the beginning of a conference devoted to various topics of scattered-light spectroscopy of liquids, held in the summer of 1971 in Paris, Keyes and Kivelson [194] listed eight theories put forward to account for the fine structure of the RLW [131, 183, 188, 194, 195, 197, 198, 200].

The authors of these theories, and authors of others who proposed different theories of the fine structure, have since developed their proposals and suggested different variants. It is not my aim to provide any complete critical account of these theories.

Purely arbitrarily, these theories can be divided into two groups: purely phenomenological theories and statistical (if the term can be used) theories.

The phenomenological theories are based on the equations of motion and on the fluctuation–dissipation theorem, whereas the statistical theories rely on calculations of the methods developed in Refs [194–200, 202]. Theoretical and experimental investigations have been continued [203, 204] and are continuing, so that a full review of the evolution of the problem would exceed the limits of my paper.

The most general formulas describing the molecular scattering spectra for various polarisations are those that follow from Rytov's phenomenological theories [183] and will be given here:

$$I_{VV} = \frac{kT}{2\pi i\omega}\left\{\frac{1}{\Delta}\left[\frac{Xq^2}{3}\left(\frac{XC}{3} - 2YC + 2ZK\alpha\right) + Y^2Cq^2 - 2YZK\alpha q^2 - Z^2(A + Bq^2)\right] + \sum_j \frac{m_j^2}{\lambda_j} + \frac{2}{3}\sum_k \frac{n_k^2}{\lambda_k} - \text{c.c.}\right\}, \qquad (76)$$

$$I_{VH} = I_{HV} = -\frac{kT}{2\pi i\omega}\left(\frac{X^2q^2}{4A} + \frac{1}{2}\sum_k \frac{n_k^2}{\lambda_k} - \text{c.c.}\right)\ , \qquad (77)$$

$$I_{HH} = \frac{kT}{2\pi i\omega}\left\{\frac{q^2}{\Delta}\left[\frac{X^2C}{2}\left(1 - \frac{\cos\theta}{3}\right) + 2X(YC - ZK\alpha)\cos\theta\right] + \frac{1}{2}\sum_k \frac{n_k^2}{\lambda_k}\sin^2\theta - \text{c.c.}\right\} + I_{VV}\cos^2\theta\ . \qquad (78)$$

Here

$$A = \mu q^2 - \rho_0\omega^2,\ \ B = K + \frac{\mu}{3}\ ,\ \ C = \frac{1}{T_0}\left(\rho_0 C_V - \frac{\kappa q^2}{i\omega}\right)\ ,$$

where μ is the shear modulus, ρ_0 is the density, κ is the thermal conductivity, K is the bulk modulus, and

$$\Delta = (A + Bq^2)C + K^2\alpha q^2\ .$$

In Rytov's theory [183] a fluctuation of the optical permittivity is described by

$$\Delta\varepsilon_{\alpha\beta} = X\,\tilde{u}_{\alpha\beta} + Yu\,\delta_{\alpha\beta} + ZT\,\delta_{\alpha\beta} + \sum_j \frac{m_j}{\lambda_j}\Xi\delta_{\alpha\beta} + \sum_k \frac{n_k}{\lambda_k}\tilde{Z}_{\alpha\beta}\ .$$

Here, $u_{\alpha\beta}$ is the strain tensor, and m_j and n_k are real constants such that

$$\frac{kT}{2\pi i\omega}\sum_j m_j^2\left(\frac{1}{\lambda_j} - \frac{1}{\lambda_j^*}\right) = \frac{kT}{\pi}\sum_j \frac{m_j^2\tau_j^2}{1 + \omega^2\tau_j^2}\ ,$$

$$\lambda_j = 1 + i\omega\tau_j\ ,$$

$$\frac{kT}{2\pi i\omega}\sum_k n_k^2\left(\frac{1}{\lambda_k} - \frac{1}{\lambda_k^*}\right) = \frac{kT}{\pi}\sum_k \frac{n_k^2\tau_k^2}{1 + \omega^2\tau_k^2}\ ,$$

$$\lambda_k = 1 + i\omega\tau_k\ .$$

The above formulas provide a full description of the spectra of light scattered by the density and anisotropy fluctuations in a medium, which is on the whole isotropic. These formulas take account of the dispersion and any number of relaxation times both of scalar and of tensor parameters.

This is the most general solution of the problem, but the formulas given in Eqns (76)–(78) are difficult to apply to experimental results. They contain many parameters representing quantities which, in principle, can be derived from independent experiments.

These theoretical formulas admit the possibility of any number of relaxation times of different origin.

The $I_{VV}(\omega)$ spectra have been discussed above quite thoroughly and the quantities which can be deduced from such spectra have been identified. Let us now consider in detail $I_{VH}(\omega, q)$ given by Eqn (77).

The experimental results can be judged and compared with the theoretical formulas if Eqn (77) for $I_{VH}(\omega, q)$ is simplified taking into account the experimental results, namely that only two anisotropy relaxation times τ_1 and τ_2 (Fig. 25) are observed in a clear manner. Eqn (77) can then be written as follows:

$$I_{VH}(\omega, q) \propto \frac{kT}{2\pi i\omega}\left[\frac{\tilde{X}^2q^2\cos^2(\theta/2)}{4(\tilde{\mu}q^2 - \rho\omega^2)} + \frac{1}{2}\left(\frac{n_1^2}{1 + i\omega\tau_1} + \frac{n_2^2}{1 + i\omega\tau_2}\right) - \text{c.c.}\right]\ , \qquad (79)$$

where $\tilde{\mu}$ and $\tilde{X}$ are the complex values of the shear modulus and of the magneto-optic coefficient, respectively:

$$\tilde{\mu} = \frac{1}{2}i\omega\left(\frac{N_1^2\tau_1}{1 + i\omega\tau_1} + \frac{N_2^2\tau_2}{1 + i\omega\tau_2}\right) = \mu + i\omega\eta(\omega)\ , \qquad (80)$$

$$\tilde{X} = i\omega\left(\frac{n_1N_1\tau_1}{1 + i\omega\tau_1} + \frac{n_2N_2\tau_2}{1 + i\omega\tau_2}\right)\ . \qquad (81)$$

The constants N and n, which occur in Eqns (79)–(81), can be expressed in terms of physical quantities such as the

static viscosity and the maximum shear modulus $\mu = \rho v_T^2$, where v_T is the velocity of transverse sound, X can be expressed in terms of the Maxwellian constant M, and $D = n_1^2/n_2^2$ is the ratio of the integral intensities of the spectral components with half-widths τ_1^{-1} and τ_2^{-1}.

If we know the six parameters needed for calculation on the basis of Eqn (79) — $\eta, \tau_1, \tau_2, \mu_\infty(\tau_M), D$, and M — calculation of this kind can be carried out on a computer. In the case of salol and benzophenone this calculation was carried out by Starunov and myself [169]. The results of this calculation will be discussed below.

The fine structure of the Rayleigh line wing, but not of the whole spectrum, can be described by making further simplifications which are not in conflict with experiments: we can assume that $n_2 = 0$ and also that $\tau_1 \gg \tau_2$ and $\omega^2\tau_1\tau_2 \ll 1$. Assumptions of this kind, which agree with experiments, modify Eqn (79) for $I_{VH}(\omega, q)$ to

$$I_{VH}(\omega, q) \propto I_0 \frac{kT}{2\pi} \left\{ \frac{\omega^2\Gamma + \omega_m^4(1-R)\Gamma^{-1}\cos^2(\theta/2)}{(\omega^2-\omega_m^2)^2+\omega^2\Gamma^2[1+\omega_m^2(1-R)\Gamma^{-2}]^2} + \frac{\Gamma\sin^2(\theta/2)}{\Gamma^2+\omega^2} \right\} . \quad (82)$$

Here

$$\Gamma = \tau_1^{-1}, \quad \omega_m^2 = q^2 \frac{\eta}{\rho}\frac{1}{\tau_1}, \quad R = \frac{1-(\tau_2/\tau_M)}{1-(\tau_2/\tau_1)},$$

where τ_M is the Maxwellian relaxation time [see Eqn (75)].

Eqn (82) is a simplified formula from the general theory [183] and is practically identical with the formulas derived from the statistical theories [193–200].

An analysis of the situation as a whole led Starunov [205, 206] to the conclusion that the fine structure is the result of the interaction of orientational motion modes with shear strains, which gives rise to a scattered-light doublet and can be described by Eqn (82).

Although Eqn (82) contains explicitly only the relaxation time $\Gamma^{-1} = \tau_1 \equiv \tau$, in fact the other times τ_2 and τ_M occur in this formula via the coupling parameter R.

Eqn (82) and its equivalents describe well the doublet structure of the spectrum, which can be seen quite clearly from Fig. 24 [158], Fig. 22 [156], Fig. 23 [157], and Fig. 21 [207] (the calculated results are represented by continuous lines). A similar good agreement is obtained in other cases, which are not cited here, but can be found in the literature [172].

It should be stressed particularly that we have considered so far the scattered-light spectra of liquids with viscosities such that the fine structure of the RLW is clearly visible in the form of a doublet or, in other words, there is a narrow dip at the exciting line frequency $\omega = 0$. The very first experiments have shown that the fine structure disappears when temperature is lowered and the viscosity increases [165]: for example, the fine structure of anisaldehyde is no longer observed at 8 cP [157]. When the experimental investigations have provided sufficiently diverse data on the dynam-ics of the spectrum of light scattered in materials each of which has a wide range of viscosities from 10^{-2} to 10^{10} P and in various substances [146, 147, 161, 162, 165–169], it has been found that the two branches in Fig. 27 can be described by a single theory which is of phenomenological nature and, therefore, does not pretend to provide a description of the spectrum throughout the full range of the viscosities [183]. Since the formulas deduced from the general theory contain six parameters, Rytov found [184] that these formulas can fully describe the phenomenon or, in other words, can account for the high- and low-temperature branches simultaneously, if these parameters are regarded as the fitting quantities.

However, the parameters of Rytov's phenomenological theory [183, 184] have a physical meaning and can be found by independent experiments, so they cease to be the fitting parameters. The necessary six quantities for salol and benzophenone have made it possible to compare the experimental results with the theoretical formulas. It has been found that the situation is not as simple as one would like.

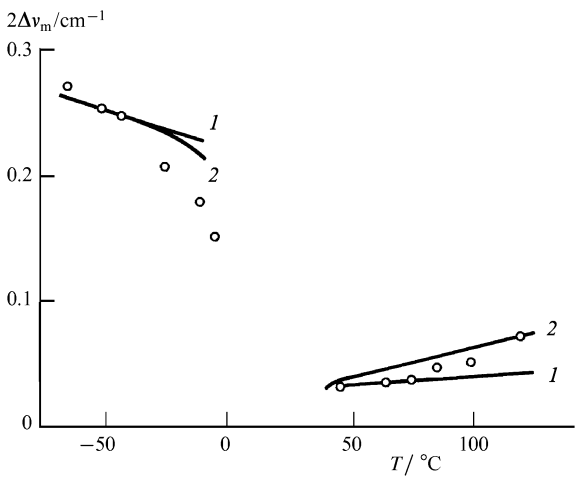

Figure 29. Temperature dependences of the separation $2\Delta\nu_{max}$ between the fine-structure components of the Rayleigh line wing of salol. Circles represent the experimental results. Curve *1* is plotted with the influence of the instrumental function neglected and curve *2* is calculated on the basis of the Lorentzian instrumental function with a half-width of 2×10^{-2} cm^{-1} [169].

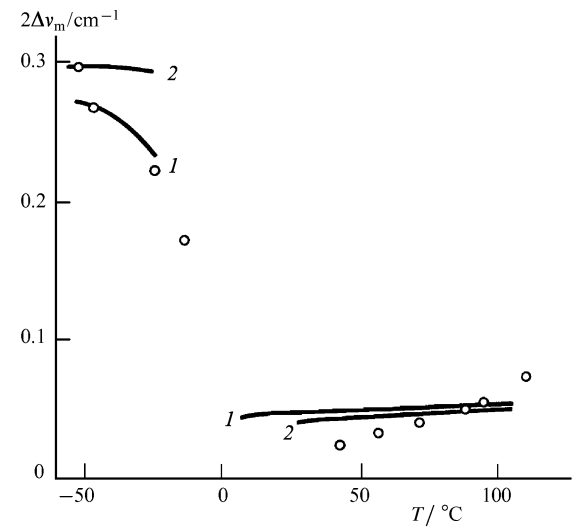

Figure 30. Dependences of the separation $2\Delta\nu_{max}$ between the maxima of the fine structure of the Rayleigh line wing of benzophenone. Circles represent the experimental results. Curve *1* is calculated for $v_T = 920$ m s^{-1} and curve *2* for $v_T = 1200$ m s^{-1}. The positions of the points are not very sensitive to the value of v_T [169].

All the necessary parameters and all the required details of the calculations can be found in Refs [45, 165–169]. Here, we shall give graphically the results of the calculations and represent the experimental results by circles or other symbols. Fig. 29 gives the data obtained for salol and Fig. 30 gives the corresponding data for benzophenone.

It is clear from these figures that the phenomenological [183] and statistical [193–200] theories both describe qualitatively and in a satisfactory manner the fine structure of the RLW.

The situation is quite different in the case of the low-temperature branch. In this case there is not even a qualitative agreement between Eqn (79), predicted by Rytov's theory [183], and experiments.

This discrepancy between the theory and experiment is evidently of the same origin as the discrepancies that result from the use of relaxation theories with local derivatives to describe the propagation of sound in a viscous medium.

It is well known that a relaxation theory with local derivatives does not predict the correct frequency dependences of the velocity and absorption of sound.

This difficulty was overcome by Isakovich and Chaban [208] in their theory of propagation of sound in viscous and highly viscous media. Their theory provides a satisfactory description of the temperature dependences of the velocity and absorption of sound, but neither this nor similar theories have been generalised to describe the spectrum of molecular light scattering.

Some attempts to develop a theory of the spectrum of light scattered in a viscous liquid have been made, but they represent only a very early stage.

Much work on the fine structure of the RLW has been done on low-viscosity liquids when a relaxation theory based on local derivatives can be applied (see, for example, Refs [208–216, 224]).

Efforts of this kind remain topical and they continue.

8.1 Modulation of light scattered as a result of transient changes in anisotropy fluctuations. Propagation of a transverse elastic wave

It follows from hydrodynamics [14, 153, 154] that the changes in the shear strains of a viscous medium with time are described by the following equation of motion:

$$\dot{\Phi}(t,r) - \frac{\eta}{\rho}\nabla^2\Phi(t,r) = 0 \ . \tag{83}$$

The solution of Eqn (83) identifies the law obeyed by time modulation of the scattered light considered from the point of view of hydrodynamics. If the solution of Eqn (83) is sought, as usual, in the form

$$\Phi(t,r) = \Phi_0 \exp[\mathrm{i}(\Omega t - \boldsymbol{q}\cdot\boldsymbol{r})] \tag{84}$$

and if Eqn (84) is substituted in Eqn (83), the result is

$$\Phi(t,r) = \Phi_0 \exp\left(-\frac{q^2\eta}{\rho}t\right)\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}) \ . \tag{85}$$

The field of the scattered optical wave, modulated by the function (85), is

$$E(t) = E_0\Phi_0 \exp\left(-q^2\frac{\eta}{\rho}t\right)\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}) \ . \tag{86}$$

It readily follows from Eqn (86) that the scattered-light intensity decreases in accordance with the exponential law

$$I(t) = I_0 \exp\left(-\frac{2q^2\eta}{\rho}\right)t \tag{87}$$

without oscillations.

Transformations similar to those described by Eqns (25)–(30) yield the following expression for the frequency distribution of the intensity

$$I(\omega) = \frac{(\delta/\pi)I_{\mathrm{VH}}}{\omega^2 + \delta_\xi^2} \ , \tag{88}$$

where the line half-width is $\delta_\xi = q^2\eta/\rho$ and the line maximum is at $\omega = 0$. Consequently, hydrodynamics predicts that the scattered-light spectrum consists of a line or band of width δ_ξ without any other discrete components.

In fact, as demonstrated above, the details of this phenomenon are much 'richer' than predicted by hydrodynamics. The spectrum of molecular scattering of light includes doublets and triplets, depending on the state of an isotropic medium.

The doublet structure of the spectrum is described well by both the phenomenological and statistical theories which contain such quantities as the velocity and absorption of a transverse or shear elastic wave, so that the theoretical expressions together with the experimental data make it possible to determine the principal characteristics of transverse sound, which are its velocity and absorption.

A detailed analysis of this situation was made by Starunov [205, 206] (see also Ref. [169]), who considered the velocity v and the absorption coefficient α at the wavelength Λ and the frequency Ω_{T}, and thus derived expressions on the assumption that there are only two anisotropy relaxation times, τ_1 and τ_2, and one Maxwellian time τ_{M}, such that $\tau_1 > \tau_{\mathrm{M}} > \tau_2$:

$$\alpha\Lambda = \frac{\alpha v}{\Omega_{\mathrm{T}}} = \sqrt{1 + \Omega_{\mathrm{T}}^2 T^2} - \Omega_{\mathrm{T}} T \ , \tag{89}$$

$$v = \sqrt{\frac{2\eta\Omega_{\mathrm{T}}}{\rho}}\left[\sqrt{\sqrt{1 + \Omega_{\mathrm{T}}^2 T^2} - \Omega_{\mathrm{T}} T}\right]K \ , \tag{90}$$

$$T = \tau_1 \frac{1 - (\tau_2/\tau_{\mathrm{M}}) + (\tau_2/\tau_1) + (\Omega_{\mathrm{T}}^2\tau_2^2\tau_1\tau_{\mathrm{M}}^{-1})}{1 + \Omega_{\mathrm{T}}^2\tau_1\tau_2(\tau_1 - \tau_{\mathrm{M}} + \tau_2)\tau_{\mathrm{M}}^{-1}} \ , \tag{91}$$

$$K = \frac{(1 + \Omega_{\mathrm{T}}^2 T^2)[1 + \Omega_{\mathrm{T}}^2\tau_1(\tau_1 - \tau_{\mathrm{M}} + \tau_2)\tau_2\tau_{\mathrm{M}}^{-1}]}{(1 + \Omega_{\mathrm{T}}^2\tau_1^2)(1 + \Omega_{\mathrm{T}}^2\tau_2^2)} \ . \tag{92}$$

The above formulas make it possible to plot the dependence of $\alpha\Lambda/2\pi$ on $\Omega_{\mathrm{T}} = 2\pi f_{\mathrm{T}}$, which is indeed done in Fig. 31. The arrow in this figure identifies the ordinate at which the doublet structure is observed. The dashed horizontal line identifies the value below which the modulating function is oscillatory and, consequently, discrete lines appear in the spectrum. Fig. 32 gives the temperature dependence of $\alpha\Lambda/2\pi$. The dashed line still gives the value of $\alpha\Lambda/2\pi$ below which the modulating function is oscillatory.

In the region where the fine structure of the RLW or the doublet structure exists in the spectrum, the modulating function ceases to be exponential, but does not yet become

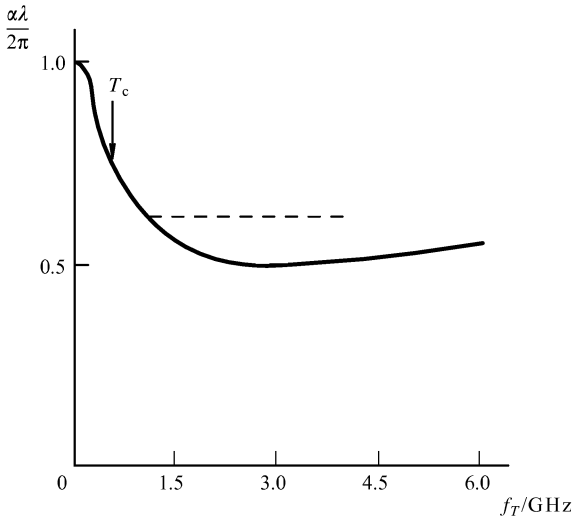

Figure 31. Dependence of $\alpha\Lambda/2\pi$ on the frequency $\Omega_T = 2\pi f_T$ representing observations of light scattered at $\theta = 90°$. An arrow identifies the value of $\alpha\Lambda/2\pi$ at which the fine structure of the Rayleigh wing appeared. The horizontal dashed line is the level below which the modulation (correlation) function $\Phi(t, q)$ is oscillatory [169].

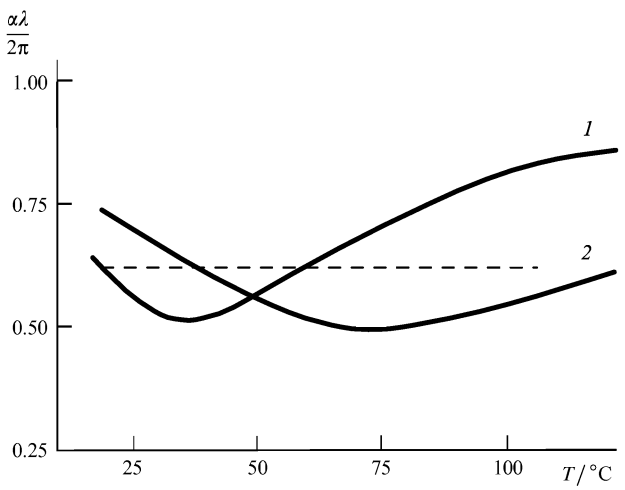

Figure 32. Temperature dependence of $\alpha\Lambda/32\pi$ for salol. Curve *1* corresponds to 0.9 GHz and curve *2* corresponds to 3 GHz [169].

regularly oscillatory, and the region where a well-resolved triplet is observed corresponds to a regularly oscillatory modulating function.

Fig. 26 shows the $I_{VH}(\omega)$ spectrum of salol for different viscosities. The results, obtained with a multipass interferometer, are recorded with a DAS-1 unit and then transferred to a personal computer where the whole block of data is analysed appropriately in accordance with a special program.

An analysis of the triplet spectrum makes it possible to use the half-widths of the shifted components in order to determine the attenuation coefficient of hypersound in salol as a function of temperature. The shifts of the discrete lines from the exciting line can be used to deduce the temperature dependence of the velocity of hypersound.

The results of such an analysis are presented in Fig. 33. The continuous curves in this figure give the results of calculations carried out on the basis of the formulas given

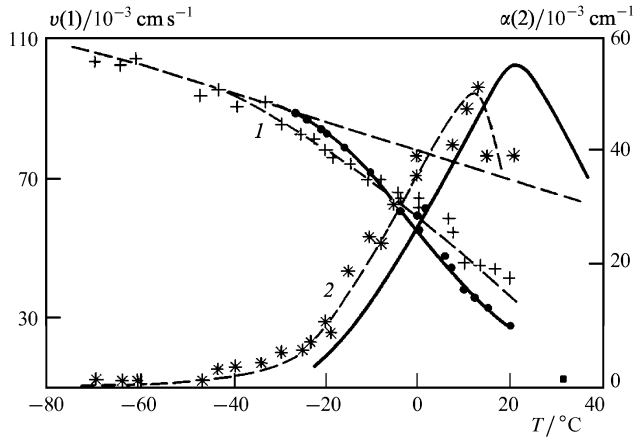

Figure 33. Temperature dependences of the absorption coefficient $\alpha(2)$ and of the velocity $v(1)$ of hypersound. The continuous curves are the results calculated on the basis of theoretical formulas [208]. Symbols connected by dashed lines are the experimental results [148].

by Isakovich and Chaban [208]. The qualitative agreement between the experimental and theoretical results can be regarded as satisfactory, but there is no quantitative match and the task of developing a satisfactory theory of the effect is still to be done.

If $\alpha\Lambda/2\pi = 1$, it follows—as shown above [see Eqns (39) and (40)]—that discrete spectral lines cannot be observed.

8.2 Spectra of depolarised light scattered by anisotropy fluctuations in the critical region

The region where phase transformations and critical phenomena take place is usually confined to a narrow range of the external parameters and represents a zone of catastrophic changes in the state of matter and of such striking phenomena as the critical opalescence. A paper by Oxtoby and Gelbart [119] stimulated new interest in the critical opalescence and in the influence of double and multiple scattering on the scattered-light characteristics. These authors suggested a new nontrivial method for determination of the absolute value of the integral intensity of the scattered light [119]. A partial account of studies of this kind can be found in reviews [98, 99] and in the literature cited in these reviews.

The behaviour of the intensity and spectra of light scattered by fluctuations of such thermodynamic quantities as the pressure, entropy, temperature, and concentration has been investigated in detail under a variety of conditions, as can be partly seen from the above account.

The situation is different in the case of the spectrum of light scattered in the critical range because of fluctuations of such an internal parameter as the anisotropy. This can be formulated as the question: how does the critical state influence the RLW or the spectrum of depolarised scattered light? And can one influence this spectrum at all?

To the best of my knowledge, until our first experimental investigations were published [217, 218], there had been no theoretical or experimental work on this topic. However, the behaviour of the anisotropy fluctuations in phase transformations is important and the spectrum of light scattered on these fluctuations can possibly provide

information on the nature of the behaviour of anisotropic molecules in the critical region.

Before the experiments were started, each of the authors of these two papers [217, 218] had his own idea about the expected behaviour of the RLW in the critical region. A solution should contain at least one of the two liquids with a strong RLW. The first solution to be investigated consisted of nitrobenzene and n-hexane. Light scattered in this solution was analysed by a Fabry–Perot interferometer with two different dispersion ranges $\Delta\nu = 1.833$ and $16.7\,\mathrm{cm}^{-1}$. The experimental results revealed a considerable narrowing of the depolarised scattering spectrum. The critical exponent in the temperature dependences of the relaxation times τ_1 and τ_2 was determined with a large error of $\sim 50\%$ (this point is discussed earlier; see also Fig. 18). For the diverging parts of the dependence this exponent proved to be about 0.6.

A qualitatively similar narrowing had been reported for an aniline–cyclohexane solution [217].

This investigation was continued [218] and nitrobenzene–n-hexane and n-dodecane–β,β'-dichlorodiethyl ether were investigated for the second time. Once again, narrowing of the depolarised spectrum was observed.

There have been other investigations of this topic [217, 219–223] and, moreover, large parts of the theses of Utarova [219] and Kolesnikov [149] dealt with the same topic.

Spectroscopic investigations in the critical region are complicated by the critical opalescence when a major role is played by double and multiple scattering of light, which leads to depolarisation of light which initially is polarised linearly in a plane perpendicular to the scattering plane. For this reason a very careful alignment of the whole system is needed so as to avoid parasitic scattering. This difficulty has been evident right from the beginning of our investigations and, therefore, special care was taken in our experiments. A description of all the details of the work done can be found in the theses of Utarova [219], Kolesnikov [149], and Sabirov [45], including a description of the apparatus used to record simultaneously the spectrum of depolarised scattered light by two Fabry–Perot interferometers with different dispersion ranges, as well as a number of other measures and precautions taken to avoid possible distortion of the experimental results by the critical opalescence.

By way of example, Fig. 34 shows the dependence of the anisotropy relaxation time τ_2 on $\varepsilon = (T - T_c)/T_c$ plotted on a logarithmic scale for a nitrobenzene–n-hexane solution. The interval $\Delta T = T - T_c$ ranged from 40 to 0.08 °C.

The part of the curve corresponding to τ_1 was not investigated, but it could be affected significantly by the light depolarised as a result of the critical opalescence and because this part was narrow. For details, see Refs [149, 219].

Two theoretical papers appeared at approximately the same time and their results could be used to describe the narrowing of the spectrum of depolarised scattered light in solutions. These were the papers of Chaban [226], who tackled the description of the observed narrowing specifically, and of Wilson [227], who presented his paper at a conference earlier and deal with a different topic. However, Wilson also discussed the behaviour of the rotational diffusion coefficient near a critical point of a solution and was thus directly relevant to the problem in question, because the anisotropy relaxation time τ and the

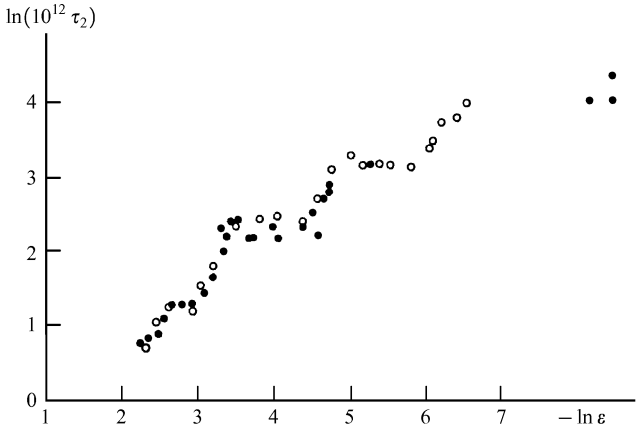

Figure 34. Dependence of the anisotropy relaxation time τ_2 (which is the reciprocal of the half-width of the Rayleigh line wing) on $\Delta T = T - T_c$, plotted on a logarithmic scale [$\varepsilon = (T - T_c)/T_c$, ΔT varies from 40 to 0.08 °C], for a nitrobenzene–n-hexane solution [218].

rotational diffusion coefficient D_r are related by the following simple expression derived from the Stokes–Debye and Einstein formulas:

$$\tau = (6D_r)^{-1} \propto (T - T_c)^{\sigma} \ . \tag{93}$$

Here, $D_r = kT/8\pi\eta r^3$. According to Wilson, in the critical region we have to replace r with r_c. The results obtained earlier lead to the expression $r_c \propto \varepsilon^{-0.63}$ and then $\tau \propto \varepsilon^{-\sigma}$, where $\sigma \sim 2$. According to Wilson, $\sigma = 3/2$.

According to Chaban's theory [226], the narrowing of the depolarised spectrum near T_c is due to the divergence of the concentration fluctuations. In this theory, the expression for the free energy includes the product of the average square of the anisotropy tensor fluctuations and the average square of the concentration fluctuations.

Chaban [226] gives the following expression for the anisotropy relaxation time:

$$\tau = (a + b\varepsilon^{\sigma})^{-1} \ . \tag{94}$$

Here, a and b are parameters which depend weakly on temperature and the critical exponent is $\sigma = 0.8$. It should be pointed out that the two expressions, (93) and (94), correspond to very different mechanisms of narrowing of depolarised light, but both may act simultaneously in real experiments.

The temperature dependences of the anisotropy relaxation time or of the reciprocal of the half-width of the RLW are different for different solutions. For example, the RLW decreases monotonically in width in the case of carbon disulfide–ethyl alcohol solutions (Fig. 35).

The narrowing is more usually nonmonotonic: this is shown, by way of example, in Fig. 36 for an n-hexadecane–β,β'-dichloroethyl ether. This figure clearly reveals two regions of rapid narrowing of the RLW, separated by a region where there is no change in the width. The part of the spectrum corresponding to τ_1 has not been investigated because of the parasitic influence of the critical opalescence. Throughout the temperature interval ΔT from 27 to 0.1 °C the width of the wing decreases by a factor of 15 compared with the change in the viscosity by a factor of 1.6 [149].

In the regions of rapid narrowing (Fig. 36) the critical exponent agrees with Eqn (93) on the assumption that $\sigma \sim 2$,

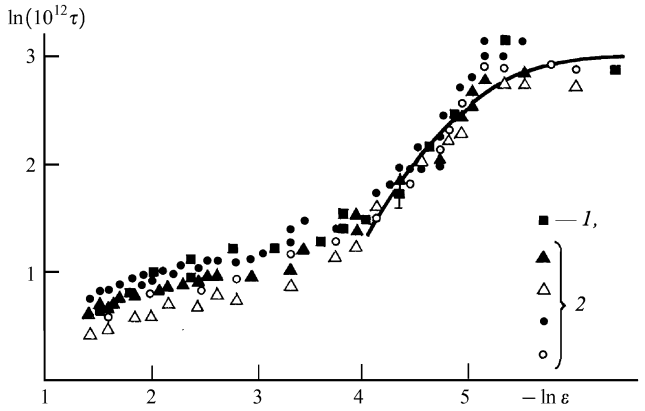

Figure 35. Dependence of $\ln\tau$ on $\ln\varepsilon$ for a carbon disulfide–ethyl alcohol solution: (*1*) τ found from the half-width of the $\nu = 656\ \mathrm{cm}^{-1}$ combination scattering line of CS_2; (*2*) remaining symbols represent the results of different analyses of the Rayleigh line wing. The continuous curve is theoretical, based on Eqn (94) with $\tau = 22 \times 10^{-12}\ (1.5 \times 10^4\varepsilon^2 + 1)^{-1}$ [220].

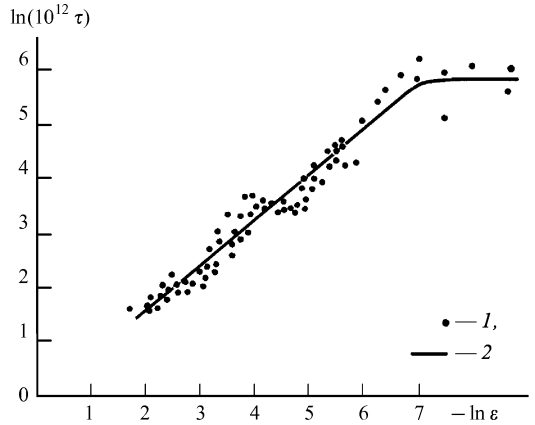

Figure 37. Dependence of $\ln\tau_2$ on $\ln\varepsilon$ for the Rayleigh line wing of an n-dodecane-β,β'-dichloroethyl ether solution. The points are the experimental results. The continuous curve is calculated on the basis of Eqn (94) of Ref. [219]; $(c\pi\tau)^{-1} = 0.018 + 5\varepsilon^{0.8}$.

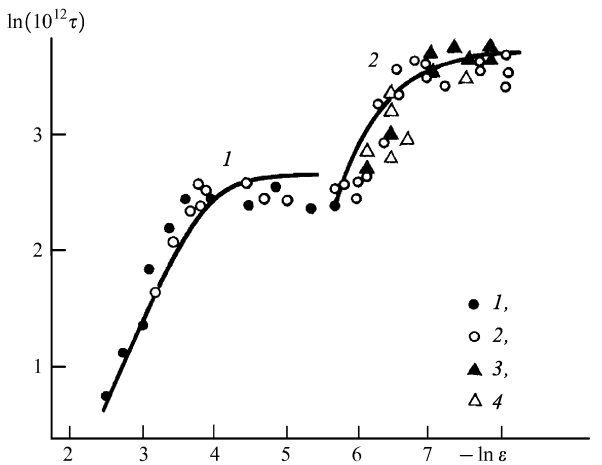

Figure 36. Dependence of $\ln\tau$ on $\ln\varepsilon$ for the Rayleigh line wing of an n-hexadiene-β,β'-dichloroethyl ether. Different symbols represent analyses of the spectra obtained for different dispersion ranges of a Fabry–Perot interferometer. The continuous curves are calculated on the basis of Eqn (94) of a theory given in Ref. [226]. (*1*) $\tau = 13.8 \times 10^{-12}\ (8.67 \times 10^2\varepsilon^2 + 1)^{-1}$; (*2*) $\tau = 39.8 \times 10^{-12}\ (2.27 \times 10^{-5}\varepsilon^2 + 1)^{-1}$ [149].

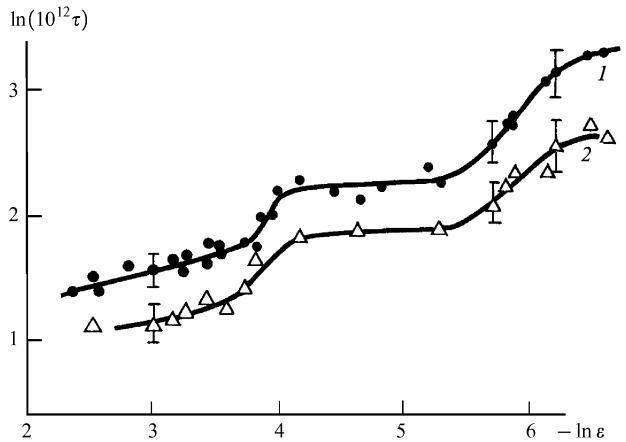

Figure 38. Dependence of $\ln\tau$ on $\ln\varepsilon$ for the Rayleigh line wing of an aniline–cyclohexane solution. The two curves (*1*, *2*) correspond to two different ways of allowing for the background [225].

but does not describe the region where there is no temperature dependence (arbitrarily called the saturation region).

However, if the nonmonotonic behaviour is ignored, as has been done in the specific case of an n-dodecane–β,β'-dichloroethyl ether solution, and a line is drawn in accordance with Eqn (94), the results are those shown in Fig. 37, where the critical exponent is $\sigma = 0.8$.

Fig. 38 shows the dependence of $\ln(10^{12}\tau)$ on $\ln\varepsilon$ for an aniline–cyclohexane solution. Curves *1* and *2* differ in respect of the treatment of the results [225]. Once again there is no doubt about the narrowing of the RLW.

It is worth noting the circumstance that depolarised Raman lines consist of a part which depends weakly on temperature and a depolarised part which depends strongly on temperature. In view of the fact that the nature of the depolarised part of a combination scattering of light (CSL) line is 'related' in its nature to the RLW, it can be assumed that the depolarised part of a CSLs line will behave in the same way as the RLW.

An investigation was therefore carried out of the temperature dependences of depolarised CSL lines of a carbon disulfide–ethyl alcohol solution. The CSL line of CS_2 at $\nu = 656\,\mathrm{cm}^{-1}$ was investigated. The temperature dependence of a line of this type is plotted in Fig. 39 where the abscissa gives both $\Delta T = T - T_c$ and T/η. It is evident from this figure that far from the critical temperature the CSL line width depends on T/η, but in the interval ΔT from 4.6 to 1.2 °C there is a significant narrowing of the CSL line although the change in the viscosity in this temperature interval is negligible. The dashed line is the result of extrapolation and the intercept on the ordinate can also be used to find the 'residual' width. This residual width has been determined for pure carbon disulfide [149].

Similar studies have also been made on depolarised Raman lines of nitrobenzene in the case of a nitrobenzene–n-hexane solution. Fig. 40 shows the width of depolarised lines of nitrobenzene at $\nu_1 = 610\,\mathrm{cm}^{-1}$, $\nu_2 = 1345\,\mathrm{cm}^{-1}$, and $\nu_3 = 1586\,\mathrm{cm}^{-1}$, plotted with the use of the same coordinates as in Fig. 39. On approach to the critical point all three lines become narrower, but unexpectedly this happens in different temperature intervals for each of the lines. So

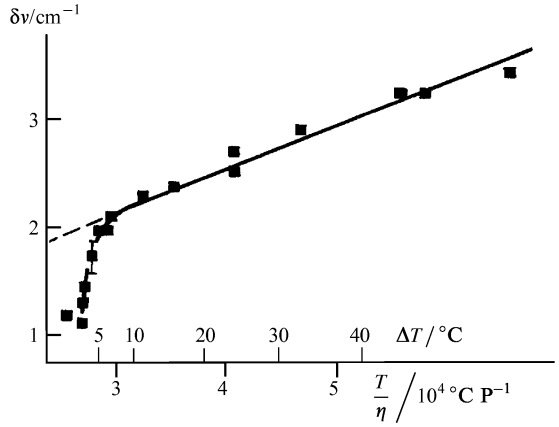

Figure 39. Dependences of the half-width $\delta\nu$ of the $\nu = 656\,\mathrm{cm}^{-1}$ depolarised Raman scattering line of CS_2 on T/η and on ΔT for a carbon disulfide – ethyl alcohol solution [220].

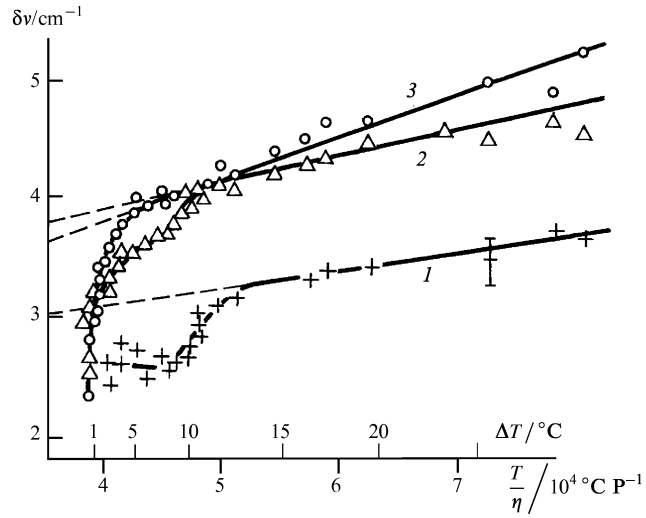

Figure 40. Dependences of the half-width $\delta\nu$ of depolarised combination scattering lines on ΔT and T/η of nitrobenzene – n-hexane solutions. The results were obtained for the following combination scattering lines: (*1*) $\nu_1 = 610\,\mathrm{cm}^{-1}$; (*2*) $\nu_2 = 1345\,\mathrm{cm}^{-1}$; (*3*) $\nu_3 = 1586\,\mathrm{cm}^{-1}$ [143, 149].

far, this has not been explained in terms of physics. An investigation of the dependences of the widths of the 610, 1345, and $1586\,\mathrm{cm}^{-1}$ lines on the value of T/η shows that throughout the whole temperature interval the dependence is linear and there are no singularities in the case of pure nitrobenzene [149, 238].

In our experiments the distribution of the intensity in the RLW has to be described by at least two Lorentzians, as demonstrated in numerous examples beginning from 1945 [132]. This has been confirmed repeatedly by various authors, as described in books [11, 144]. The same two Lorentzians apply to the lines in the case of solutions and sometimes there are three Lorentzians.

As pointed out above, different Lorentzians vary in different ways with temperature (viscosity), so that the result is a fairly complex dynamics of changes in the intensity distribution in the RLW with temperature. Studies of the narrowing of the RLW or of the depolarised part of a Raman line are best carried out on solutions in which at least one of the components consists of anisotropic molecules. The complex 'interplay' of the Lorentzians with temperature may create the illusion that the spectrum remains constant if only a part of it is studied. Nitroethane – isooctane [228] and nitromethane – n-amyl alcohol [229] solutions show no narrowing of the RLW. Publication of the first studies of the temperature dependence of the RLW in critical solutions has been followed by communications from Beysens et al. [230], who carried out some experiments that have resulted in a misunderstanding. They described the RLW for a solution by a single Lorentzian, whereas at least two were observed. Moreover, the intensity increased as a result of cooling, which could not be explained if the narrowing of the RLW were rejected. This is in conflict with experiments and theories of scattered light in general. Some investigations have also been carried out by other authors [231, 232]. A detailed analysis of the investigations that have failed to reveal the narrowing of the RLW can be found in theses [149, 219, 229] and in a detailed treatment [225].

The RLW undoubtedly originates from changes in the anisotropy fluctuations with time. The main role in these changes is played by the rotational motion of anisotropic molecules. If in the critical region there is no change in the spectrum, it should mean that the rotational motion of the molecules does not 'sense' a phase transition in this region. Moreover, the results of such an experiment carried out by Beysens et al. [230] are in conflict with the theory [226, 227], whereas the results of other experiments [217, 218, 220 – 223, 225, 238] can be regarded as being in qualitative agreement with these theories. An unsatisfactory situation exists when not only experiments are in conflict with the theory, but also experiments reported by different groups of authors disagree even in the case of the same solution.

All this means that new experiments with improved apparatus are needed on the topic in question and more extensive theoretical studies than hitherto are required of the behaviour of molecular rotation in the vicinity of a phase transition in the critical region.

Some important results were obtained some time ago [233 – 237], but the behaviour of the rotational motion of anisotropic molecules in the critical region has, to my knowledge, been discussed only by Wilson [227].

It seems to me that the rotational motion of anisotropic molecules in the critical region is an interesting and important topic.

Further work on this topic should take account, in calculations and particularly in the design of experiments, of a new type of scattering predicted and calculated by Andreev [239].

This new type of scattering, not observed (so far) experimentally lies in the spectral range outside the Rayleigh scattering (unshifted line) and is superimposed on the RLW region. This scattering originates from fluctuations of the distribution function of the thermal fluctuations. The wave vectors of the scattered light are then less than the reciprocal of the interparticle distances and greater than the reciprocal of the exciting light wavelength. Both polarised and depolarised processes occur in such scattering.

It is important to stress that Andreev reaches the following conclusion on the basis of his investigation [239]: "It is clear, however, that the mechanism discussed above should give rise to the critical opalescence in the case of depolarised scattering if the fluctuating quantity x is the

critical exponent η." According to the Landau theory, for the intensity of scattering at the critical point [13] the extinction coefficient h is

$$h = \frac{\Omega_s^4}{216\pi^2 c^4} \frac{(ab^3)^{-1/2}}{\varepsilon^2} \left(\frac{\partial\varepsilon}{\partial\eta}\right)^4 . \tag{95}$$

Here, Ω_s is the frequency of the scattered light; b is a constant; a depends on temperature as $T - T_c$ in the limit $T \to T_c$. The spectral distribution of the intensity predicted by Andreev [239] is

$$\frac{\partial h}{\partial\omega} = \frac{\Omega_s^4 |\omega|^{1/2}\omega}{216\pi^2 c^4 \varepsilon^2(\omega)} \left[\left(\frac{\partial\varepsilon}{\partial\rho}\right)_S^4 v^4 T^2 \left(\frac{2\rho}{\gamma_1^3}\right)^{1/2} + \left(\frac{\partial\varepsilon}{\partial S}\right)_P^4 \frac{C_P^2}{2\rho^2\chi^{3/2}}\right] . \tag{96}$$

Here, ω is the frequency shift, v is the velocity of sound,

$$\gamma_1 = \left[\frac{4}{3}\eta + \eta' + \chi(\gamma - 1)\right] ,$$

and the rest of the notation is standard.

All the discussions and calculations mentioned above apply only to those fluctuations, representing optical inhomogeneities, whose effective size is much less than the wavelength of light. The scattering indicatrix for light depolarised because of the scattering by the anisotropy fluctuations is then symmetric for the scattering angles θ and $180° - \theta$.

Zaitsev and Starunov [240] determined the dependence of the intensity ratio $I_\theta/I_{108°-\theta}$ on the shift of the frequency ω in the spectrum of depolarised light scattered in benzene, toluene, salol, and some other liquids.

Fig. 41 gives the results obtained for three liquids. In the case of benzene up to $20\,\mathrm{cm}^{-1}$ the ratio $I_\theta/I_{180°-\theta}$ is unity, but at higher frequencies this ratio changes and it is found that the forward scattering is stronger than the backward effect between 20 and $90\,\mathrm{cm}^{-1}$. Asymmetry appears in salol only at 120 °C and at room temperature the intensity ratio is unity throughout the frequency range. To my knowledge, this is the only investigation of this kind and various possible explanations can be put forward. One of these explanations postulates that during multiple times $t \propto 1/\omega$, fluctuations with effective dimensions of the order of the wavelength of light may appear. The number of such fluctuations is not small, but they do not survive for long: accord-ing to Ref. [240] their lifetime ranges from 2×10^{-11} to 5×10^{-13} s.

This experimental and theoretical problem may provide new information on the kinetics of fluctuations and deserves further study.

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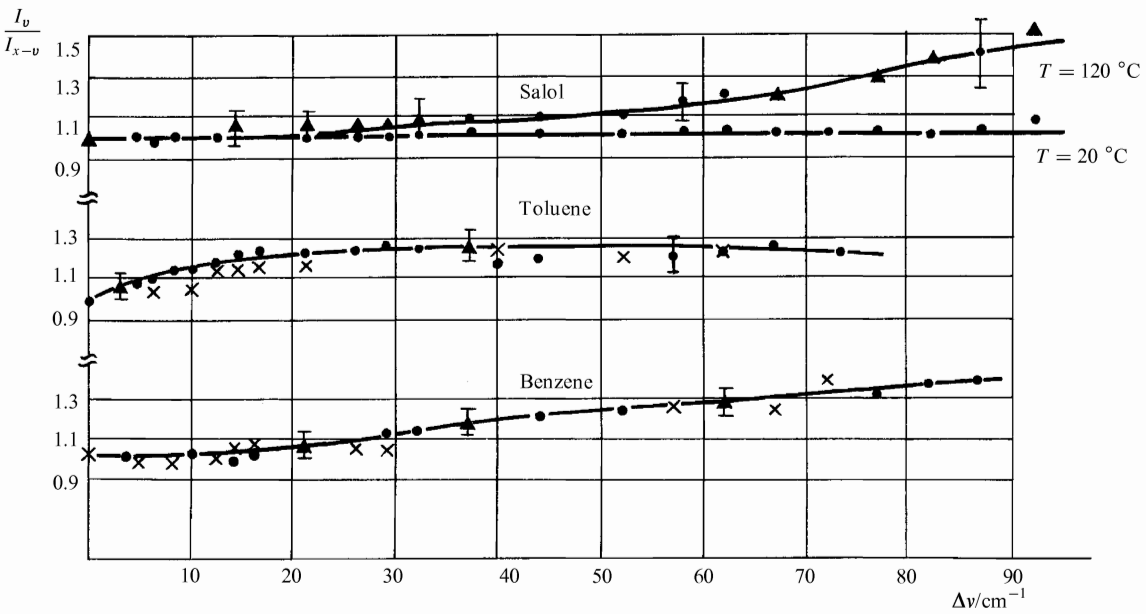

Figure 41. Asymmetry of the angular dependence of the intensity of light scattered into the wing of the Rayleigh line, $I_0/I_{180°-0}$, plotted as a function of the frequency for three liquids.

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