

Methodological Remarks

LINE WIDTH IN THE SPECTRUM OF SCATTERED LIGHT

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THE question of the width of spectral lines is a large chapter in classical and modern optics and spectroscopy (see, e.g., [1,2]). Usually one deals with emission or absorption lines, while the broadening of the lines of scattered light is much less frequently considered. Yet the study of the line width of scattering, both Rayleigh [3] and Raman [4], is of considerable interest, which has increased particularly as the result of the extensive use of lasers as light sources. For this reason, the possibilities of using light scattering for the investigation of solids have greatly increased [5].

The foregoing would justify the publication of a special review devoted to the line width of scattered light. It would be desirable to have such a review published as soon as possible, and for this purpose, incidentally, it would be necessary to consider and analyze many problems in greater detail than in the original literature known to us. The purpose of the present article, however, is much more modest, it consists merely of discussing the physical nature that distinguishes scattering line widths from emission and absorption line widths, using several simple examples. Such a problem, of course, is predominantly methodological, but the interest in it is justified in light of the long history of the question. Thus, in the thirties, a number of articles dealt with the line width of Rayleigh scattering of light in gases in an utterly erroneous manner, but subsequently the situation was seemingly straightened out in principle [6]. Recently, however, the confusion with respect to the light-scattering line width has found its reflection in the literature both in the case of Raman scattering of light in crystals with formation of excitons (polaritons) and, to a certain degree, also in classical calculations of the line width of Raman scattering of light for a molecule model [7]. By the same token, this demonstrates the psychologically understandable long lives of certain misunderstandings. It seems curious to this author that grounds were produced for discussing this question [8] thirty years after the publication of [6]. In connection with the last remark we recall, to be sure, how L. D. Landau reacted when some lecturer mentioned in his seminar the evolution of his own understanding of the discussed problem, why he occupied himself in this question, etc. In such cases, Landau always reminded the lecturer: "Don't forget that your biography interests only your wife." How true and correct this is...on the one hand! Who is interested, in fact, in the fact that in this case the author understood in 1940 certain errors and published the note [6], and then was surprised in 1971 to encounter a related question? On the other hand, however, is not the repeated insufficient understanding of physics of some particular process a

symptomatic effect, and does not the mention of the author's personal experience contribute to a clarification of the character and the very content of the article written by him? It is hardly possible to give here an unequivocal answer, which will be provided by the readers themselves, depending on their tastes and use. We now proceed to the gist of the matter.

1. EMISSION LINE WIDTH

Let us stop to calculate the optical emission line width using the classical and extensively employed example of a damped oscillator (see, e.g., [1], Sec. 85). The corresponding equation of motion is as follows:

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0. \tag{1}$$

Assume that the oscillator has an initial displacement  $x_0$  at the instant  $t = 0$ , i.e., we use the solution ( $\varphi$  is an arbitrary phase)

$$\left. \begin{aligned} x(t) &= x_0 e^{-\frac{\gamma}{2}t} \cos(\omega_R t + \varphi), & \omega_R^2 &= \omega_0^2 - \frac{\gamma^2}{4} & (t \geq 0), \\ x(t) &= 0 & & & (t < 0). \end{aligned} \right\} \tag{2}$$

Expanding the oscillation (2) in a Fourier integral

$$x(t) = \int_{-\infty}^{+\infty} x_\omega e^{i\omega t} d\omega, \quad x_\omega = \frac{1}{2\pi} \int_{-\infty}^{+\infty} x(t) e^{-i\omega t} dt, \tag{3}$$

we obtain

$$x_\omega = -\frac{x_0}{4\pi} \left\{ \frac{e^{i\varphi}}{-(\gamma/2) + i(\omega_R - \omega)} + \frac{e^{-i\varphi}}{(\gamma/2) - i(\omega_R + \omega)} \right\}. \tag{4}$$

The intensity (power) of the dipole radiation, as is well known, is proportional to  $(e\ddot{x})^2$ , where  $e$  is the particle charge. Therefore, obviously, the spectral density of the intensity  $I(\omega)$  is proportional to  $\omega^4 |x_\omega|^2$ . We shall also assume that the phase  $\varphi$  is arbitrary, and average over the phase, bearing in mind that we are observing the radiation of an aggregate of oscillators with arbitrary phases. Then

$$I(\omega) = A\omega^4 \overline{|x_\omega|^2} = \frac{Ax_0^2\omega^4}{16\pi^2} \left\{ \frac{1}{(\omega_R - \omega)^2 + (\gamma^2/4)} + \frac{1}{(\omega_R + \omega)^2 + (\gamma^2/4)} \right\} = \frac{Ax_0^2\omega^4 (\omega_0^2 + \omega^2)}{8\pi^2 [(\omega^2 - \omega_0^2)^2 + \gamma^2\omega^2]}, \tag{5}$$

where  $A$  is a certain proportionality coefficient and the averaging is denoted by a superior bar. If, as is usually the case (exception in radio band),

$$\gamma \ll \omega_0, \tag{6}$$

then we have with sufficient accuracy

$$I(\omega) = \frac{Ax_0^2\omega_0^4}{16\pi^2 [(\omega - \omega_0)^2 + (\gamma^2/4)]} = \frac{\gamma I_0/2\pi}{(\omega - \omega_0)^2 + (\gamma^2/4)}, \tag{7}$$

$$I_0 = \int_0^\infty I(\omega) d\omega.$$

Formula (7) is indeed customarily used and its meaning is quite clear. On the other hand, in the case of the more general formula (5) it is seen (see below) that  $x_0^2$  is not expressed in simple fashion in terms of  $\bar{x}^2 = \int |x_\omega|^2 d\omega$ , and consequently the assumption that  $x_0$  is constant for all the oscillators is perfectly arbitrary and unreasonable (see below). Both for this reason, and for the purpose of the subsequent exposition, let us consider a more realistic problem, i.e., the same oscillator but acted upon by a random force  $f(t)$ :

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = f(t) = \int_{-\infty}^{+\infty} f_\omega e^{i\omega t} d\omega. \quad (8)$$

Hence

$$x_\omega = \frac{f_\omega}{-\omega^2 + \omega_0^2 + i\gamma\omega}. \quad (9)$$

The role of the force  $f$  can be played, for example, by collisions that maintain the square of the oscillator amplitude at a certain unchanged average level. If we assume that  $f(t) = \sum_m a_m \delta(t - t_m)$ , then  $f_\omega = (1/2\pi) \times$

$\sum_m a_m \exp(-i\omega t_m)$ , and for random (uncorrelated)

collisions the mean value is  $\overline{|f_\omega|^2} = (1/4\pi^2) \sum_m a_m^2$ . Furthermore, in this case\*

$$\bar{x}^2 = \int_{-\infty}^{+\infty} |x_\omega|^2 d\omega = \overline{|f_\omega|^2} \int_{-\infty}^{+\infty} \frac{d\omega}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2} = \frac{\pi \overline{|f_\omega|^2}}{\gamma \omega_0^2}. \quad (10)$$

By the same token, the average values of  $\bar{x}^2$ , and consequently of the potential energy  $m\omega_0^2 \bar{x}^2/2$ , and also of the kinetic energy  $m\dot{x}^2/2$ , turn out to be constant at a given  $\overline{|f_\omega|^2} = \text{const}$  (in thermal equilibrium, these mean values are equal to  $kT/2$ ). Therefore the use of expression (9), rather than (4), is not only simpler and more convenient, but also better reasoned. From (9), taking the foregoing into account, we obtain immediately

$$I(\omega) = A\omega^4 \overline{|x_\omega|^2} = \frac{A\omega^4 \overline{|f_\omega|^2}}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2}. \quad (11)$$

Of course, expression (11) goes over into (7) under the condition (6). In the general case, however, as noted, the spectral density (11) has been obtained under more reasonable and natural assumptions than expression (5). As to the broadening of the emission and absorption lines under real conditions, and not for the simplest model under consideration, there are many possibilities and variants in this respect (see<sup>[2]</sup>).

## 2. LINE WIDTH OF RAYLEIGH AND RAMAN SCATTERING OF LIGHT IN GASES

Let us consider now the same harmonic oscillator, but acting as a scatterer rather than a spontaneous emitter of light. We assume that the incident light is monochromatic, i.e., that the field of the incident wave is

$$E(t) = \int_{-\infty}^{+\infty} E_\omega e^{i\omega t} d\omega = E_0 e^{i\omega_e t}, \quad E_\omega = E_0 \delta(\omega - \omega_e), \quad (12)$$

with the frequency  $\omega_e$  located far from resonance. What will be the spectral composition of the scattered light if

account is taken of the damping of the scattering oscillator, or under conditions when the spontaneous emission of the oscillator experiences impact broadening (in the latter case, under the simplest assumptions, we obtain formula (7) with  $\gamma = 2/\tau$ , where  $\tau$  is the average time between collisions; see<sup>[1,2]</sup>)? This question has been answered in a number of articles (for a bibliography see<sup>[6,11]</sup>) as follows: the scattering line width will be the same as in the case of emission; a similar answer was obtained by the author also in many private discussions. Yet it is easy to see that under our assumptions the scattered light will be monochromatic, i.e., there is practically no line broadening. Indeed, the equation of motion of an oscillator in the field (12), which is assumed directed along the  $x$  axis, is

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = f(t) + \frac{e}{m} E_0 e^{i\omega_e t}. \quad (12a)$$

Hence

$$x_\omega = \frac{\frac{e}{m} E_0 \delta(\omega - \omega_e) + f_\omega}{-\omega^2 + \omega_0^2 + i\gamma\omega}, \quad (13)$$

and far from resonance, i.e., at  $|\omega_e - \omega| \gg \gamma$ , and also under the assumption that the collisions do not occur too frequently, the absolutely predominant term is the one proportional to  $\delta(\omega - \omega_e)$ , since the random force  $f_\omega$  has by assumption a broad spectrum.

The foregoing is clear, of course, also without any spectral resolution: when the light is scattered, the oscillator executes forced oscillations having the same frequency as the driving force (the scattered wave). The collisions, on the other hand, so long as their duration  $\Delta\tau$  can be neglected, alter the amplitude and phase of the oscillator's natural oscillations of frequency  $\omega_c = \sqrt{\omega_0^2 - (\gamma^2/4)}$ , which is assumed to be significantly different from the frequency  $\omega_e$  of the incident wave. During the time  $\Delta\tau$ , when another system already scatters, the scattering changes, and this leads, in particular, to a depolarization of the scattered light<sup>[12]</sup>.

Broadening appears, of course, also when resonance is approached (a separate analysis, although quite clear in principle, is needed also for the scattering of a succession of pulses rather than a monochromatic wave).

Far from resonance, and neglecting the duration of the collisions in comparison with the free path time, the scattering line broadening is connected only with the motion of the scatterer (such a conclusion was confirmed by a quantum calculation<sup>[11]</sup>). The first to appear here is the usual Doppler broadening<sup>[1,2,6]</sup>

$$I(\Omega) = \text{const} \cdot e^{-\Omega^2/b^2}, \quad \Omega = \omega - \omega_e, \quad b^2 = \frac{8kT\omega_e^2 \sin^2(\theta/2)}{Mc^2}, \quad (14)$$

where  $\theta$  is the scattering angle and  $T$  the temperature of the scattering gas, which consists of particles (aggregates of oscillators) of mass  $M$ .

There exists in addition a broadening genetically connected with Doppler broadening, but with an intensity proportional to the square of the pressure. This effect was considered in<sup>[6]</sup> for a rarefied gas with a free path  $l > \lambda_0/2 \sin(\theta/2)$ , and  $\lambda_0 = 2\pi c/\omega_e$ . In this case, the intensity in the line wing (in the region  $\Omega \gg b$ ) is  $I(\Omega) = \text{const} \cdot p^2/\Omega^6$ , where  $p$  is the pressure. The discussed broadening is due to the fact that collisions change the projection of the velocity of the atom (oscillator) along the observation direction. The Doppler

\*A more exact calculation of the mean values can be found in [9], Sec. 121. Similar reasoning as applied to an electric circuit can be found in [10].

shift of the frequency therefore also changes, i.e., the derivative of the phase becomes discontinuous, or in other words, the scattered wave consists of sections with different frequencies, although with a continuous phase. Naturally, the Fourier expansion of such a wave has an additional "wing," the intensity of which increases with increasing pressure\*.

The region of pressures where  $l \sim \lambda_0/2 \sin(\theta/2)$  is intermediate and is difficult to analyze. On the other hand, if  $l \ll \lambda_0/2 \sin(\theta/2)$  (compressed gas) then, just as in the case of condensed media, a phenomenological approach is possible; concretely, the Rayleigh scattering is described as scattering by acoustic and entropy waves (see<sup>[3]</sup>). In this case, the question of the scattering line width has already been considered long ago<sup>[13-15,3]</sup>. The scattering line width in a condensed medium will be discussed in the next section of this article, and now we proceed to the line width of Raman scattering of light in gases.

The customarily employed classical model used to describe Raman scattering of light by a molecule is an oscillator (generalized coordinate  $x$ , say proportional to the distance between the two nuclei in a diatomic molecule) which simulates the electronic polarizability of the molecule  $\alpha(x)$ :

$$p(t) = \alpha(x) E = \alpha(x) E_0 e^{i\omega_e t}, \quad \alpha(x) = \alpha(0) + \left(\frac{d\alpha}{dx}\right)_0 x, \quad (15)$$

where  $p$  is the dipole moment of the molecule induced by the incident field  $E$  (for details see<sup>[1,4]</sup>).

The change of the coordinate  $x$  can be described, in a certain approximation, by Eq. (8). Then, according to (3), (8), and (15)

$$p_a = \alpha(0) E_0 \delta(\omega - \omega_e) + \left(\frac{d\alpha}{dx}\right)_0 \frac{f_\Omega}{-\Omega^2 + \Omega_0^2 + i\gamma\Omega} = p_{\omega_e} + p_\Omega, \quad \Omega = \omega - \omega_e, \quad (16)$$

where, to standardize the notation, the oscillator frequency  $\omega_0$  in (8) is now designated  $\Omega_0$ . The first term in  $P_\omega$  is responsible for the Rayleigh scattering and is not of interest to us now. Therefore the spectral density of the Raman scattering can be written in the form

$$I(\Omega) = A\omega_e^4 |p_\Omega|^2 = \frac{(\gamma\Omega_0^2/\pi) I_0}{(\Omega^2 - \Omega_0^2)^2 + \gamma^2\Omega^2}, \quad I_0 = \int_{-\infty}^{+\infty} I(\Omega) d\Omega, \quad (17)$$

where we have put  $\omega = \omega_e$ , which is legitimate if  $\Omega \ll \omega_e$ ; it is also assumed that  $|f_\Omega|^2 = \text{const}$ . The frequency region  $\Omega < 0$  corresponds to a red satellite, and the region  $\Omega > 0$  to a violet satellite. If  $\Omega_0 \gg \gamma$ , then we have for each of the satellites

$$I(\Omega) = \frac{\gamma I_0/4\pi}{(\Omega - \Omega_0)^2 + (\gamma^2/4)^2}, \quad \Omega_0 \gg \gamma, \quad \Omega = \omega - \omega_e, \quad (18)$$

\*If the gas consists of atoms of different sorts (with different masses), then the broadening under discussion contains also a term proportional to  $\Omega^{-4}$ . Additional broadening is produced also in the presence of collision that transform the atoms (molecules) into states with different polarizabilities. We note, finally, that in the case of degenerate levels of the scattered molecule scattering connected with transitions of the molecule from the given sublevel to other sublevels of the level under consideration is superimposed on the Rayleigh (coherent) scattering. In fact, we are dealing here with Raman scattering that is already accompanied by line broadening (see below).

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where  $I_0$  is the total intensity of both satellites. In the case of an emission or absorption line, the condition  $\omega_0 \gg \gamma$  (see (6)) is always satisfied in optics, so that the general formula (11) has no real value in the optical band, and expression (7) is always more convenient in broadening of suitable type. On the other hand, in the case of scattering, the region of applicability of formula (17) is much broader, since the frequency  $\Omega_0$  can be low, as is certainly the case for certain oscillations, for example on approaching a second-order phase transition point (see<sup>[16,17]</sup> and the next section of the article).

We have derived above for the emission line width not only expression (11) but also expression (5). If, as is sometimes done also for Raman-scattering lines, we proceed in analogous fashion, i.e., we do not introduce the Raman force  $f(t)$  but write in (15)

$$x = x_0 e^{-\frac{\gamma}{2}t} \cos(\Omega_R t + \varphi), \quad \Omega_0^2 = \Omega_0^2 - \frac{\gamma^2}{4}, \quad (19)$$

then the Fourier expansion for

$$p(t) = \left(\frac{d\alpha}{dx}\right)_0 x E_0 e^{i\omega_e t}$$

leads to a formula of the type (5)

$$I(\Omega) = \frac{A'\omega_e^4 (\Omega_0^2 + \Omega^2)}{(\Omega^2 - \Omega_0^2)^2 + \gamma^2\Omega^2}. \quad (20)$$

This is just the type of an expression given in<sup>[7]</sup>, where it is considered to be more accurate than (17). However, as we have seen in Sec. 1, the situation is in fact reversed, and within the framework of the assumed model it is necessary to use (17) and not (20). We note that in<sup>[7]</sup> they also obtained an incorrect expression for the emission-line intensity (we have in mind formula (8) of<sup>[7]</sup>), which differs from the foregoing expression (5) as a result of an error made in<sup>[7]</sup> in the course of the differentiation of expression (2) with respect to time without allowance for the discontinuity of this function at  $t = 0$ ; we have avoided this error by putting  $(\ddot{x})_\omega = \omega^2 x_\omega$ .

Since the result (17) for the Raman scattering line width, as already mentioned, is analogous to formula (11) for the emission line width, an impression may be gained that the essential difference between the emission and scattering line widths is limited to the case of Rayleigh scattering. We shall show, however, that this conclusion would be too hasty, and it actually pertains only to the simplest cases, and in particular to the discussed oscillator models, which describe to some degree the scattering of light in gases. If we deal with any scattering in a condensed medium, we encounter in general a great difference between the line widths of the absorption (emission) and scattering.

### 3. SCATTERING LINE WIDTH IN LIQUIDS AND SOLIDS (RAYLEIGH SCATTERING, RAMAN SCATTERING WITH FORMATION OF POLARITONS)

Light scattering in sufficiently rarefied gases is characterized by independence (incoherence) of scattering by different volumes, or, as can be assumed, by different molecules (scattering oscillators). For dense gases and condensed media, particularly in the analysis of the spectral composition of scattered light, the scattering at different points cannot be regarded as independent. In these cases, an adequate picture, the use of

which dates back to Einstein's well known 1910 paper (see<sup>[18]</sup>), is the concept of scattering by spatial Fourier components of the dielectric-tensor fluctuations, or the essentially related analysis of the interaction of different plane waves propagating in a crystal (see<sup>[3-5,15,17]</sup>)\*.

We denote the wave vectors of the incident and scattered light by  $\mathbf{k}_e$  and  $\mathbf{k}_s$ , and the corresponding frequencies by  $\omega_e$  and  $\omega_s$ . Assuming that the medium is transparent at the frequencies  $\omega_e$  and  $\omega_s$ , we take all the quantities  $\mathbf{k}_e$ ,  $\mathbf{k}_s$ ,  $\omega_e$ , and  $\omega_s$  to be real. Then the scattered wave, say the Fourier component of the fluctuation variation of the dielectric constant  $\Delta\epsilon$  (we are considering Rayleigh scattering without allowance for anisotropy; for details see<sup>[3,14,15]</sup>), is characterized by a frequency  $\Omega$  and a wave vector  $\mathbf{q}$  given by

$$\Omega = \omega_e - \omega_s, \quad \mathbf{q} = \mathbf{k}_e - \mathbf{k}_s. \quad (21)$$

If the change of the frequency  $\Omega$  is small, then  $\mathbf{k}_s \approx \mathbf{k}_e = 2\pi n/\lambda_0 = \omega_e n(\omega_e)/c$  and

$$\mathbf{q} \approx \frac{2\pi}{\lambda_0} \sin \frac{\theta}{2} = \frac{2\omega_e n(\omega_e)}{c} \sin \frac{\theta}{2}, \quad (22)$$

where  $n(\omega_e)$  is the refractive index at the frequency  $\omega_e \approx \omega_s$  and  $\theta$  is the scattering angle.

Under the discussed conditions, the intensity of the scattering in the volume  $V$ , per unit solid angle, is equal to

$$\left. \begin{aligned} I_{\mathbf{k}_s} &= I_0 \left( \frac{V}{4\pi} \right)^2 \left( \frac{2\pi}{\lambda_0} \right)^4 |\overline{\Delta\epsilon_{\mathbf{q}}}|^2 \sin^2 \varphi, \\ \Delta\epsilon_{\mathbf{q}} &= \frac{1}{V} \int \Delta\epsilon(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \end{aligned} \right\} \quad (23)$$

where  $I_0$  is the intensity (flux) of the incident light,  $\varphi$  is the angle between the electric vector of the incident wave and the observation direction, and the averaging (superior bar) is of the type customarily employed in statistical physics.

The spectral composition of the scattered light is determined by the kinetics of the fluctuations  $\Delta\epsilon_{\mathbf{q}}$ , and specifically

$$I(\Omega) = A |\overline{\Delta\epsilon_{\mathbf{q}, \Omega}}|^2, \quad \epsilon_{\mathbf{q}, \Omega} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \Delta\epsilon_{\mathbf{q}}(t) e^{-i\Omega t} dt. \quad (24)$$

In a rather good approximation,  $\Delta\epsilon_{\mathbf{q}} = (\partial\epsilon/\partial\rho) \mathbf{T} \Delta\rho_{\mathbf{q}}$ , where  $\rho$  is the density; the density fluctuations  $\Delta\rho$  are resolved in turn into pressure fluctuations  $\Delta p$  and entropy fluctuations  $\Delta S$ :

$$\overline{(\Delta\rho)^2} = \left( \frac{\partial\rho}{\partial p} \right)_S^2 \overline{(\Delta p)^2} + \left( \frac{\partial\rho}{\partial S} \right)_p^2 \overline{(\Delta S)^2}.$$

The adiabatic (isentropic) density fluctuations, which are proportional to  $\Delta p$ , vary with time in accordance with the equations of hydrodynamics, while the kinetics of the isobaric fluctuations (which are proportional to  $\Delta S$ ) are determined by the heat-conduction equation. We shall not stop in detail to derive all the corresponding formulas (see<sup>[3]</sup>, and also<sup>[13-15]</sup>), but we shall nevertheless make a few remarks in this connection.

If we assume both the viscosity coefficients  $\eta$  and  $\zeta$ , and also the heat-conduction coefficient  $\kappa$ , to be equal to zero, then the sound propagates in the liquid without absorption, and the entropy fluctuations do not die out. In such cases, one would observe in the spectrum of the

scattered light a triplet of unbroadened lines—at the center of the line with unshifted frequency  $\omega = \omega_e$  (in which case  $\Omega = \omega - \omega_e = 0$ ), and the Mandel'shtam-Brillouin doublet  $\Omega = \pm\Omega_0$ , with  $\Omega_0 = uq = (2u\omega_e/c) \times \sin(\theta/2)$ , where  $u$  is the speed of sound of frequency  $\Omega_0$ . In quantum language, the appearance of the satellites  $\Omega = \pm\Omega_0$  is described as scattering of light accompanied by emission of a phonon with energy  $\hbar\Omega_0$  and momentum  $\hbar\mathbf{q} = (\hbar\Omega_0/u)\mathbf{q}/q$  (red satellite) or absorption of a similar phonon (violet satellite).

If we do not neglect viscosity and thermal conductivity, then the sound attenuates, and the entropy fluctuations die out, as a result of which all the triplet ions broaden. The kinetics of the isobaric fluctuations is determined by the heat-conduction equation

$$\frac{\partial T}{\partial t} - \chi \Delta T = f^T(t, \mathbf{r}), \quad \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad \chi = \frac{\kappa}{\rho c_p}, \quad (25)$$

where  $f^T$  are random "forces" due to thermal motion in the liquid; the fluctuations of  $T$  at a given pressure are proportional to the fluctuations of the entropy  $S$ , and lead in final analysis to fluctuations of the density  $\rho$  and of the permittivity  $\epsilon$  (see above).

We therefore obtain from (24) and (25)

$$\left. \begin{aligned} I_{\text{imag}}(\Omega) &= A |\overline{f_{\mathbf{q}, \Omega}^T}|^2 = \frac{(\gamma/2\pi) I_0}{\Omega^2 + (\gamma^2/4)}, \\ \gamma &= 2\chi q^2 = 4 \left( \frac{\omega_e n}{c} \right)^2 \chi (1 - \cos \theta), \quad I_0 = \int_{-\infty}^{+\infty} I_{\text{imag}}(\Omega) d\Omega, \end{aligned} \right\} \quad (26)$$

where, as below, we assume that the frequency dependence of  $|\overline{f_{\mathbf{q}, \Omega}^T}|^2$  is negligible. In the case of the Mandel'shtam-Brillouin components, corresponding to scattering by adiabatic fluctuations, we shall disregard certain fine points connected with the dispersion of sound (see<sup>[16]</sup>), and will use therefore the following equation for the pressure (see<sup>[3]</sup>):

$$\frac{\partial^2 p}{\partial t^2} - u^2 \Delta p - \Gamma \Delta \frac{\partial p}{\partial t} = f^p(t, \mathbf{r}), \quad \Gamma = \frac{1}{\rho} \left\{ \frac{4}{3} \eta + \zeta + \frac{\kappa}{c_p} \left( \frac{c_p}{c_v} - 1 \right) \right\}. \quad (27)$$

Hence

$$\left. \begin{aligned} I_{\text{ad}} &= \frac{(\gamma/2\pi) \Omega_0^2 I_0}{(\Omega^2 - \Omega_0^2)^2 + \gamma^2 \Omega^2}, \\ \Omega_0 = uq &= \frac{2u\omega_e n}{c} \sin \frac{\theta}{2}, \quad \gamma = \Gamma q^2, \quad I_0 = 2I_0^{\text{MB}} = \int_{-\infty}^{+\infty} I_{\text{ad}}(\Omega) d\Omega, \end{aligned} \right\} \quad (28)$$

where  $I_0^{\text{MB}}$  is the total intensity of one satellite; for narrow lines (at  $\gamma \ll \Omega_0$ ) we have for each of the satellites

$$I^{\text{MB}}(\Omega) = \frac{(\gamma/2\pi) I_0^{\text{MB}}}{(\Omega - \Omega_0)^2 + (\gamma^2/4)}, \quad I_0^{\text{MB}} = \int_{-\infty}^{+\infty} I^{\text{MB}}(\Omega) d\Omega, \quad (29)$$

$$\frac{\gamma}{2} = \frac{q^2}{2\rho} \left\{ \frac{4}{3} \eta + \zeta + \frac{\kappa}{c_p} \left( \frac{c_p}{c_v} - 1 \right) \right\}, \quad q^2 = 2 \left( \frac{n\omega_e}{c} \right)^2 (1 - \cos \theta).$$

The obtained formulas coincide, apart from the notation, with well known expressions (see<sup>[3,13-15]</sup>; in the book<sup>[15]</sup>, for example,  $\gamma$  is used to denote the quantity  $\gamma/2$  in (26) or (29)). We presented the derivation of these formulas, nevertheless, in order to emphasize a fact usually left obscure, namely the use of forced rather than free solutions of the equations of motion (we have in mind here Eqs. (25) and (27)). Yet, if we were interested in the propagation of sound in a liquid, then we would use in this approximation the equation

$$\frac{\partial^2 p}{\partial t^2} - u^2 \Delta p - \Gamma \Delta \frac{\partial p}{\partial t} = 0, \quad (30)$$

the solution of which for a monochromatic plane wave

\*One can single out especially the interesting question of the narrowing of Raman lines in gases with increasing pressure, but then it is still possible to consider scattering by individual molecules<sup>[38]</sup>.

with real  $q$  is given by

$$\begin{aligned} p &= p_0 e^{i(\Omega_q t - \mathbf{q} \cdot \mathbf{r})} = p_0 e^{-\frac{\gamma}{2} t} e^{i(\Omega'_q t - \mathbf{q} \cdot \mathbf{r})}, \\ \Omega_q &= \Omega'_q + i \frac{\gamma}{2}, \quad \gamma = \Gamma q^2, \quad \Omega'_q = \sqrt{\Omega_0^2 - \frac{\gamma^2}{4}}, \quad \Omega_0^2 = u^2 q^2. \end{aligned} \quad (31)$$

If we assume on the other hand, in accordance with another possible formulation of the problem, the frequency  $\Omega_q$  to be real, then the wave vector  $\mathbf{q}$  will be complex, since Eq. (30) leads only to a general connection (dispersion equation)

$$\Omega_0^2 - u^2 q^2 - i \Gamma \Omega_q q^2 = 0. \quad (32)$$

In the case of scattering of light, both quantities  $\Omega$  and  $q$  in (21) are real, since  $\mathbf{k}$ ,  $\mathbf{k}'$ ,  $\omega_e$ , and  $\omega_s$  are real. Such "sound" waves can propagate in a medium only because we are dealing with forced solutions of (27). The dispersion equation, obviously, does not apply to forced solutions of (27). The dispersion equation, obviously, does not apply to forced solutions. Thus, when account is taken of sound absorption, it is in general wrong to speak of light scattering with absorption or emission of a phonon—what is absorbed or emitted is not a sound wave capable of freely propagating in a given medium, but a certain forced acoustic perturbation, with frequency  $\Omega$  and wave vector  $q$  as defined in (21). The foregoing does not prevent us, generally speaking, from using measurements of the scattering line width to determine the absorption coefficient of hypersound. Indeed, by determining from (28) or (29) the quantity  $\gamma$ , we also obtain by the same token the coefficient  $\Gamma$  or  $\gamma$  for the propagation of sound (see (31)). But the situation is so simple only by virtue of neglecting the dispersion of sound, i.e., the frequency dependence of the viscosity and heat-conduction coefficients. In strong absorption and in the general case this cannot be done at all, and the determination of the velocity and of the damping of the hypersound (i.e., the investigation of the dispersion equation  $F(\Omega_q, \mathbf{q}) = 0$  for the propagation of sound) by the light-scattering method may turn out to be difficult. A similar situation obtains also in other cases, for example in the scattering of light in crystals with formation of excitons (see<sup>[8]</sup> and below).

A very interesting and unique case of light scattering takes place near second-order phase-transition points or near the point of a first-order phase transition close to a second-order transition. This question has been discussed already quite long ago<sup>[5,16,17,20-23]</sup>, but unfortunately still remains insufficiently clear. On one hand, there is no doubt of the existence of particle fluctuations and of unique opalescence near second-order phase transition points. This pertains, in particular, to the  $\alpha \rightleftharpoons \beta$  transition in quartz, at which anomalous scattering of x-rays<sup>[24]</sup> and neutrons<sup>[25]</sup> is also observed. On the other hand, no account was taken in the theory<sup>[16,17,20,22]</sup> of the possible appearance of twins\*,

\*The calculations in [16,17,20,22] are based on the Landau theory of phase transitions, which is inaccurate near the transition point itself. However, as already emphasized in [17,20], a theory of the Landau type has apparently a much larger region of applicability when it comes to the scattering of light than in the case of calculations of the specific heat or scattering of x-rays and neutrons, accompanied by a large change in the wave vector (in the case of light scattering, the wave vector of the light changes by an amount  $q = (2n\omega_e/c) \sin(\theta/2) \lesssim 4\pi/\lambda_0 \lesssim 3 \times 10^5 \text{ cm}^{-1}$ ).

and in the experiments with quartz<sup>[21,23]</sup> the relative role of the scattering by fluctuations of the ordering parameter and by microtwins also remains unclear. The problem of scattering of light near points of second-order phase transitions (and related first-order transitions) is undoubtedly worthy of further experimental and theoretical study. Why it does not attract the necessary attention is something we cannot understand and is more likely due to some random causes.

In the last few years there has been increasing research on Raman scattering of light in solids accompanied by production of different excitations such as excitons, polaritons, magnons, etc. (see<sup>[4,5,8,26-32]</sup>). This group of questions deserves a special review\*. We shall stop to discuss here only the line width for scattering with formation of polaritons (real excitons), since the corresponding analysis<sup>[8]</sup> is quite closely related to the preceding part of the present article.

The term "polariton" or, more rarely, "real exciton" is customarily used to describe excitons propagating in crystals and considered with allowance for delay; this means essentially that we are dealing with "normal" electromagnetic waves or photons in a medium (for details see the literature indicated above, and also<sup>[33-35]</sup>). Scattering of light with formation of polaritons (and, concretely, one polariton), neglecting damping of the polaritons, constitutes scattering in which there is emitted (or absorbed) in the medium a "normal" electromagnetic wave—a polariton with frequency  $\Omega$  and wave vector  $q$  satisfying the conditions (21). In other words, the process under discussion is perfectly analogous to scattering with formation of Mandelstam-Brillouin satellites in liquids (solids), except that the phonons are replaced by polaritons (real excitons)†.

We confine ourselves for simplicity to an optically isotropic medium† and neglect spatial dispersion. Then the optical properties of the medium are characterized by a dielectric constant  $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ . Just as in the case of Rayleigh scattering above, we shall assume that the medium is transparent to the incident and scattered waves with frequencies  $\omega_e$  and  $\omega_s$ . This means that  $\epsilon(\omega_e)$  and  $\epsilon(\omega_s)$  are real quantities, i.e., we can put  $\epsilon''(\omega_e) = \epsilon''(\omega_s) = 0$ . As to a scattering wave with fre-

\*This question was the subject of an international conference in 1968, the proceedings of which were published [5]. In July 1971, the second international conference devoted to light scattering in solids was held in Paris, and judging from the program it reflected the exceedingly vigorous and extensive development of the corresponding research. The proceedings of the conference will be published and a reference to them is given (see [32]), although the author could naturally not be acquainted with them.

†The introduction of the term "real exciton" is due to the fact that other excitons are also considered, for example Coulomb excitons and mechanical excitons (see [33-35]). We emphasize also that the terminology in this field has not yet been standardized, something that must be borne in mind when becoming acquainted with the literature.

‡The "three-photon" process discussed here (we are dealing here with interaction of three waves or three photons with frequencies  $\omega_e$ ,  $\omega_s$ , and  $\Omega$  in a medium), is possible only in a medium without a symmetry center, but such media include also non-gyrotropic cubic crystals of the class  $T_d \equiv \bar{4}3m$  (ZnS, ZnSe, etc.), which are optically isotropic if one disregards effects of spatial dispersion of higher order (this means that  $\epsilon_{ij}(\omega, \mathbf{k}) = \epsilon(\omega)\delta_{ij}$ ).

quency  $\Omega = \omega_e - \omega_s$ , its absorption, generally speaking, cannot be neglected.

The dispersion relation for a wave of frequency  $\Omega$  propagating freely in a medium is

$$\frac{c^2 q^2}{\Omega^2} = (n - i\kappa)^2 = \epsilon(\Omega) = \epsilon'(\Omega) - i\epsilon''(\Omega). \quad (33)$$

This, of course, is the usual expression relating  $\Omega$  with  $q$  in the case of propagation of transverse electromagnetic waves in an isotropic medium. By virtue of (33), the "normal" (free) waves propagating in the medium in any direction  $z$  are

$$E = E_0 \exp \left\{ -\frac{\Omega}{c} \kappa z + i \left( \Omega t - \frac{\Omega}{c} n z \right) \right\}, \\ n = \sqrt{\frac{\epsilon'}{2} + \sqrt{\left(\frac{\epsilon'}{2}\right)^2 + \left(\frac{\epsilon''}{2}\right)^2}}, \quad \kappa = \sqrt{-\frac{\epsilon'}{2} + \sqrt{\left(\frac{\epsilon'}{2}\right)^2 + \left(\frac{\epsilon''}{2}\right)^2}}. \quad (34)$$

As a result of the presence of absorption (i.e., under the condition  $\epsilon''(\Omega) \neq 0$ ), the normal waves (polaritons) are absorbed, and, for example, at a real frequency  $\Omega$ , the wave vector  $q$  in the normal waves is complex. But in scattering of light with formation of polaritons, the latter should, by virtue of (21), have real  $\Omega$  and  $q$ . The seeming contradiction is eliminated if it is recalled that the scattering is an induced process\* and the dispersion equation (33) has no relation to the "polaritons" produced in scattering†. In other words, only if absorption is neglected can we speak in the literal sense of Raman scattering with production of polaritons. If absorption is taken into account, what is produced is not a free polariton but a certain polariton-like wave. The latter does not prevent us, of course, from using Raman scattering of light for the study of polaritons. The situation in this respect is analogous to that already discussed in connection with Rayleigh scattering in liquids. Concretely, for scattering with formation of "polaritons" we obtain a formula for the line width<sup>[8,28]</sup>  $I(\Omega, q)$ , which contains the same parameters that determine also the propagation of "normal" electromagnetic waves—polaritons. For certain further details and the formula for the scattering line width itself we refer the reader to<sup>[8]</sup>, the contents of which need hardly be discussed here, since it is easily available. We note only the fact that in<sup>[8]</sup> we did not introduce the random "forces"  $f(t, r)$ , the consideration of which is particularly convenient in the classical approach to the scattering problem. Instead, the equation for the polariton field in<sup>[8]</sup> contains in explicit form a "force" that takes into account the action of the electric fields of the incident and scattered waves on the medium. Such an approach, which is equivalent to a consideration of the energy of interaction of the incident and scattered waves

\*The fact that a certain difficulty was seen here is clear, for example from the articles [26] and [28]. Thus, in [26] an attempt was made to connect  $\Omega$  and  $q$  at the maximum of the Raman scattering line by the relation  $c^2 q^2 / \Omega^2 = n^2$ ; in [28], the relation  $c^2 q^2 / \Omega^2 = \epsilon'(\Omega)$  is discussed. This is done in both cases in order to obtain a real quantity in the right-hand side of the dispersion equation. Such an approach does not lead to agreement with observations and, more importantly, it is essentially incorrect, since  $\Omega$  and  $q$  in the "polariton" produced upon scattering are not connected at all by a dispersion equation.

†We have in mind here any scattering, including spontaneous scattering, and not only the so-called stimulated scattering produced when waves of high intensity are scattered [3,4,36,37].

with an acoustic or exciton waves produced (absorbed) as a result of scattering, is natural in those cases when it is necessary or advantageous to carry out the calculation of the intensity within the framework of quantum theory.

The examples presented in this section have apparently demonstrated the unique nature of the question of the line width of light scattering, as compared with the line width of light absorption or sound absorption, which is determined by the free propagation equation of the corresponding waves. Thus, for example, the polariton absorption line is produced when the crystal absorbs an incident free wave with frequency  $\Omega$  (of course, to obtain the line it is necessary to change the frequency  $\Omega$ ), i.e., it reduces to a determination of the absorption coefficient  $\kappa(\Omega)$  which enters in the dispersion equation (33).

The problem of the line width of light scattering (especially one bears in mind also stimulated Raman and Rayleigh scattering<sup>[36,37]</sup>), let alone the scattering of electromagnetic waves in a plasma and by relativistic particles) is quite important and has many aspects. It has remained in the past somewhat in the shadow in connection with purely experimental difficulties, namely the lack of suitable sources of monochromatic light, which has particularly hindered a broad development of research on the scattering line width. Now, using lasers, this obstacle has been eliminated, and this has already led to the above mentioned impressive development of various researches on light scattering in all possible media. In particular, the spectral composition (width) of scattering lines are being investigated more and more frequently, and one can assume that this tendency will remain in force and become stronger. The author hopes in this connection that the present article will be useful, although it did not touch upon many concrete problems in the theory of scattering line width in different media.

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